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BOUNDARY LAYER
AND CHEMICAL REACTIONS

by B. V. Alekseyev

Computer Center, Academy of Sciences USSR
Moscow, 1967

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PREFACE

In recent years a new science (aerothermochemistry) has been /3
formed at the junction of such sciences as, for example, the kinetic
theory of gases, chemical kinetics and gas dynamics. This science
is concerned with the study of gas flows at great velocities when
chemical conversions are possible. Since rocket technology has
developed so rapidly, we are confronted with the problem of shield-
ing instruments from heat at very high temperatures. The process
of ablation involving heat-protective material is a rather complex
one. This process may involve fusion, fusion with evaporation of
the melted coating, sublimation, surface combustion and the mechan-
ical and heat erosion of the fairing.

A strict mathematical formulation of the above problems re-
quires solving nonlinear parabolic equations of a hypersonic boundary
layer with boundary conditions on the moving surfaces, where gen-
erally speaking, there may be several. Often the surface temperature
or the degree of gasification given as the boundary conditions,
must also be determined as a result of solving this problem. This
paper is devoted to formulating problems and the numerical solution
to equations of a chemically nonequilibrium boundary layer. All
the numerical calculations have been made from a sample of heat-
protective carbon. The numerical results obtained by calculating
the frozen and equilibrium boundary layer are also compared with
the results of calculating the chemically nonequilibrium boundary
layer. We have studied the effect from a model of molecular re-
actions on the parameters of the boundary layer and the discrepan-
cies in the experimental data with respect to the pressure of sat-
urated carbon vapors. In the calculations we have taken into account
the final reaction rate on the surface of the covering and in the
pores of the material. In making the numerical calculations we
tried to use formulas and numerical values for the transfer coef-
ficient, the chemical reaction constant, etc., that are possibly
more precise. However, with the appearance of new and more refined
information about these values, the numerical results of course
may be improved. At the present time virtually no educational lit- /4
erature or monographs exist on aerothermochemistry. Therefore, we
decided to present the problems of aerothermochemistry, indicated
above, in considerable detail.

The author wishes to express his appreciation to Anatoliy
Alekseyevich Dorodnitsyn for the suggested theme, for extremely
valuable advice during its development, and for constant attention
to the project.

CONVENTIONAL SYMBOLS

x_i -Cartesian coordinates

$\vec{v}_0$ -mean mass gas velocity;

c_α -mass concentration of the α-component in a mixture of gases;

$j_{\alpha i}$ -component vector of the diffusion current of the α-component in a gas mixture;

R_α -mass velocity of the formation of the α-component as a result of all the reactions in the gas phase;

p, ρ, T -pressure, density, and temperature, respectively.

t -dimensionless temperature $t = T/T_e$;

h_α -complete enthalpy of the α-component, $h_\alpha = h_\alpha^0 + \int_0^T c_{p\alpha} dT$;

R -universal gas constant;

$D_{\alpha\beta}$ -binary diffusion coefficient;

$\varkappa$ -thermal conductivity coefficient of the mixture;

Pr -Prandtl number of the mixture;

ε -blackness coefficient of the surface;

σ -Stefan-Boltzmann constant;

$k_f (k_b)$ -velocity constant of a direct (inverse) reaction;

$\nu'_\alpha, \nu''_\alpha$ -stoichiometric coefficients;

A_α -symbol for the α-chemical component in gas mixture;

M_α -molecular weight of the α-component;

N_α -Avogadro's number;

η -viscosity coefficient of the mixture;

K_p -equilibrium constant calculated on the basis of the partial pressure of the components;

s, n -coordinates connected with the generatrix of the body;

Ψ -current function;

u, v -vector components of the mean mass velocity in the coordinates;

c_p -heat capacity of the mixture at a constant pressure;

Λ, L -Lewis numbers;

k -Boltzmann constant;

A -sticking probability;

Δ^*, Δ^{**} -displacement width, pulse loss width;

m_α — molecular mass of the α-component;

n_α — number of α-component molecules per unit volume;

T^* — reduced temperature;

L — heat of sublimation;

E — activation energy of the reaction;

Q_l — heat of the l-th reaction;

r — mean statistical radius of the pores.

Subscripts and other symbols.

The subscript "e" refers to the values of functions on the outer edge of the boundary layer and subscript "w" refers to the values of functions on the surface of the body.

In the numerical calculations, number subscripts have been used for concentrations: C_1 - C, C_2 - CO, C_3 - CO_2, C_4 - O, C_5 - O_2, C_6 - N, C_7 - N_2, C_8 - NO.

A line generally signifies that the pertinent value characterizing the α-component in a gas mixture refers to the molecular weight M_α. Latin subscripts ordinarily refer to vector components in the Cartesian system and Greek subscripts refer to components of the gas mixture. The other symbols and subscripts are defined in the text.

CHAPTER 1

ELEMENTS OF THE KINETIC THEORY OF GASES

1. Boltzmann Equations

Let us look at the dynamic behavior of a system of monatomic particles. We know from classical mechanics that the dynamic state of a system at any a priori given moment of time is determined entirely by which coordinates and particle impulses are assigned at the initial moment of time. A system having n degrees of freedom is usually determined by the variables $p_1, \ldots, p_n$ and $q_1, \ldots, q_n$, where q_i represents the generalized coordinates and p_i represents the impulses corresponding to them, which are determined by the equations

$$p_i = \partial L / \partial \dot{q}_i,$$

(1.1.1)

where $\dot{q}_i = dq_i/dt$, $L = T - U$. Here L is the Lagrangian, $T(\dot{q}, q)$ is the kinetic energy, $U(q)$ is the potential energy. Both here and below the absence of a subscript in the variables means that the function generally depends on the complete set of independent variables. If the system consists of N particles (a value usually on the order of 10^{23}) then for particles not having internal degrees of freedom (rotations, vibrations, etc.), $n = 3N$, since for each particle, three translational degrees of freedom are required. Thus, it is actually impossible to give a complete description of the state of a complex macroscopic system. In a statistical definition the concept of an ensemble of dynamically similar systems is used. The state of a system at a given moment of time can be represented by a point in the phase $6N$-dimensional space of a gas which is a combination of configuration space and pulse space. The position of the system in configuration space is determined by $\vec{r}^N (\vec{r}_1, \ldots, \vec{r}_N)$ and in the pulse space the pulse of the system is given by the vector $\vec{p}^N (\vec{p}_1, \ldots, \vec{p}_N)$. However, in a statistical definition, it is not the movement of one single representative point in the phase space of the gas that is studied, but that of an entire

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*Numbers in the margin indicate pagination in original foreign text.

combination of phase points which represent a set of possible states of the system. Such a combination of phase points is called an ensemble. The state of such an ensemble is determined by the
distribution function $f^N(\vec{r}^N, \vec{p}^N, t)$, which is the probability phase
density. A change in the function f^N versus time, as we know, can
be described by the Liouville equation which is a generalized equa-
tion of continuity. However, this equation has $6N$ independent
variables and is difficult to solve. Thus in formulating kinetic
equations we use distribution functions of a much lower order,
primarily of the first $f^{(1)}(\vec{r}, \vec{p}, t)$, and only in studying high
density gases are we concerned with a distribution function of the
second order $f^{(2)}(\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2, t)$.

Let there be a gas consisting of μ components. Let us then
call the independent variable $\vec{r}, \vec{v}_\alpha, t$ the distribution function[1]
$f_2(\vec{r}, \vec{v}_\alpha, t)$ so that the value
$$dn_\alpha = f_\alpha(\vec{r}, \vec{v}_\alpha, t) d\vec{r}\, d\vec{v}_\alpha$$

$$(\alpha = 1, ..., \mu; \quad d\vec{r} = dx_1 dx_2 dx_3; \quad d\vec{v}_\alpha = dv_{1\alpha} dv_{2\alpha} dv_{3\alpha}), \qquad (1.1.2)$$

for the moment of time t, is the mathematical expectation of the
number of atoms of the α-component which have the coordinates ξ_i
and velocity projections $\lambda_{i\alpha}$ that satisfy the inequalities

$$x_i \leq \xi_i \leq x_i + dx_i; \quad v_{i\alpha} \leq \lambda_{i\alpha} \leq v_{i\alpha} + dv_{i\alpha} \quad (i = 1, 2, 3). \qquad (1.1.3)$$

It is obvious that the set of functions f_α is sufficient for des-
cribing a gas whose properties are independent of the relative
position of two or more particles. Thus, the following discussion
is valid for a sufficiently rarefied gas in which the sizes of the
molecules are small in comparison with their mean path, while the
time of influence of the intermolecular forces during collision is
small in comparison with the time of molecular movement between
collisions. In addition, let us assume that the contribution of
triple collisions is small and does not noticeably affect the type
of distribution function. If the gas is found in the force field
$m_\alpha \vec{F}_\alpha$ which acts on α-type molecules the simplifying assumption is
then natural that these forces are small in comparison with the
forces acting on the molecules at the time of collision.

At the moment of time t there are $f_\alpha(\vec{r}, \vec{v}_\alpha, t)\, d\vec{r}\, d\vec{v}_\alpha$ molecules
per volume element $d\vec{r}$ around point $\vec{r}$, if the velocities of the
molecules are in the range $\vec{v}_\alpha, d\vec{v}_\alpha$ [2]. If no collisions occur, at

[1] There is no reason to examine a single-particle distribution func-
tion for the entire gas, since the component molecules of the mix-
ture possess different masses and mean velocities.
[2] Both here and below the expression "molecules $\vec{v}_\alpha, d\vec{v}_\alpha$" signifies (as
in [1]): "molecules of α-type, whose velocities are in the range
$\vec{v}_\alpha, \vec{v}_\alpha + d\vec{v}_\alpha$".

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the moment of time $t + dt$ all these molecules would then be in a volume $d\vec{r}$ around point $\vec{r} + \vec{v}_\alpha dt$ with velocities in the range of $\vec{v}_\alpha + \vec{F}_\alpha dt, d\vec{v}_\alpha$. Their number $f_\alpha(\vec{r} + \vec{v}_\alpha dt, \vec{v}_\alpha + \vec{F}_\alpha dt, t + dt)$ would coincide with the initial ones. However, as a result of collisions some of the molecules from the first group do not enter the second group, while some of the molecules not found in the first group at the moment of time t do enter the second group. In a multicomponent gas in which chemical reactions take place, two types of collisions are possible: elastic collisions during which no exchange of energy occurs between the internal and translational degrees of freedom, and inelastic collisions in which such an exchange does occur. Below we assume that the internal energy of the molecules is accumulated only from the translational energy and the potential chemical energy h_α^0 the value of which depends on the chemical affinity between the specific gases. The other forms of internal energy (rotations, vibrations) have not been studied. Then the absolute increase in the number of molecules of the α-component in the second group is proportional to $d\vec{r}\, d\vec{v}_\alpha dt$ but equal to $(\frac{\partial_e f_\alpha}{\partial t} + K_\alpha) d\vec{r}\, d\vec{v}_\alpha dt$ where the first term represents elastic, and the second term inelastic, collisions. Thus:

$$[f_\alpha(\vec{r}+\vec{v}_\alpha dt, \vec{v}_\alpha+\vec{F}_\alpha dt, t+dt) - f_\alpha(\vec{r}, \vec{v}_\alpha, t)] d\vec{r} d\vec{v}_\alpha =$$

$$= \left(\frac{\partial_e f_\alpha}{\partial t} + K_\alpha\right) d\vec{r} d\vec{v}_\alpha dt. \qquad (1.1.4)$$

The left-hand side of this equation can be expanded into a Taylor series near the point $(\vec{r}, \vec{v}_\alpha, t)$:

$$\frac{\partial f_\alpha}{\partial t} + \sum_{i=1}^{3} v_{\alpha i} \frac{\partial f_\alpha}{\partial x_i} + \sum_{i=1}^{3} F_{\alpha i} \frac{\partial f_\alpha}{\partial v_{\alpha i}} = \frac{\partial_e f_\alpha}{\partial t} + K_\alpha, \quad \alpha = 1, \dots, \mu. \qquad (1.1.5)$$

It is obvious that the equation for a free molecular stream can be written in the form

$$\frac{\partial f_\alpha}{\partial t} + \sum_{i=1}^{3} v_i \frac{\partial f_\alpha}{\partial x_i} + \sum_{i=1}^{3} F_{\alpha i} \frac{\partial f_\alpha}{\partial v_i} = 0. \qquad (1.1.6) \underline{/9}$$

Let us obtain expressions for $\partial_e f_\alpha/\partial t$ under conditions of molecular chaos when the relative positions and speed of two molecules prior to collision have no statistical dependence and such a dependence is created only after collision. To obtain accurate expressions for the collision terms [the right-hand side of equations (1.1.5)] we must know the nature of the molecular reactions during collision. Experiments show that molecules at distances exceeding the molecular dimensions attract one another poorly, but at distances close to the molecular dimensions they are strongly repelled. During elastic collisions it is natural to consider the molecule as the center

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of a spherical, symmetrical, force field which has the potential

$$\chi = \frac{\lambda}{r^n} - \frac{\beta}{r^m},$$

where r is the distance between the two given particles n and m; λ and β are positive constants with $n > m$. Simpler models of molecular reaction have been studied. One of the simplest models is the concept of a molecule as a smooth and absolutely elastic sphere. Maxwell investigated a case when the reaction force between molecules was a repulsion force that is inversely proportional to the fifth power of the distance. In this case the collision integral is clearly independent of the relative molecular velocity.

Thus, let us investigate the elastic collision of two molecules, whose masses are m_α and m_j. Prior to collision when there is still no noticeable interaction between them, let the velocities of the particles be $\vec{v}_\alpha, \vec{v}_j$, and after collision let them be $\vec{v}'_\alpha, \vec{v}'_j$. Let us introduce the symbols $m_0 = m_\alpha + m_j$; $M_\alpha = m_\alpha/m_0$; and $M_j = m_j/m_0$ and write the equation of the conservation of momentum:

$$m_\alpha \vec{v}_\alpha + m_j \vec{v}_j = m_\alpha \vec{v}'_\alpha + m_j \vec{v}'_j.$$

(1.1.8)

Here we have used the condition of conservation of mass of the particles: $m_\alpha = m'_\alpha, m_j = m'_j$, since we have studied that portion of the collisions that does not result in chemical reaction. From equation (1.1.8) it follows that, at the time of the collision, the center of the masses moves at a constant velocity $\vec{G}$:

$$\vec{G} = M_\alpha \vec{v}_\alpha + M_j \vec{v}_j.$$

(1.1.9)

Let us introduce the relative velocities $g_{j\alpha}, g'_{j\alpha}, g_{\alpha j}, g'_{\alpha j}$ which are, respectively, the initial and final velocities of the molecule j relative to a molecule of the $\alpha(g_{j\alpha}, g'_{j\alpha})$-type and, conversely $(g_{\alpha j}, g'_{\alpha j})$. Thus by definition

$$\vec{g}_{j\alpha} = \vec{v}_j - \vec{v}_\alpha = -\vec{g}_{\alpha j}; \quad \vec{g}'_{j\alpha} = \vec{v}'_j - \vec{v}'_\alpha = -\vec{g}'_{\alpha j}.$$

(1.1.10)

Thus, the values for the vectors $g_{j\alpha}$ and $g_{\alpha j}$ as well as $g'_{j\alpha}$ and $g'_{\alpha j}$ are equal pairwise. Let us show that the values for all these vectors are equal to one another. In fact the law of conservation of energy gives

$$\frac{1}{2}(m_\alpha v_\alpha^2 + m_j v_j^2) = \frac{1}{2}(m_\alpha v'^2_\alpha + m_j v'^2_j).$$
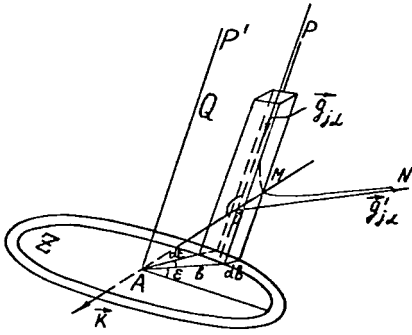
(1.1.11)

But, as is easily seen:

$$\vec{v}_\alpha = \vec{G} + M_j \vec{g}_{\alpha j}; \quad \vec{v}_j = \vec{G} + M_\alpha \vec{g}_{j\alpha}; \qquad (1.1.12)$$

$$\vec{v}'_\alpha = \vec{G} + M_j \vec{g}'_{\alpha j}; \quad \vec{v}'_j = \vec{G} + M_\alpha \vec{g}'_{j\alpha}. \qquad (1.1.13)$$

Using (1.1.12) and (1.1.13) we obtain:

$$m_\alpha v_\alpha^2 + m_j v_j^2 = m_0 (G^2 + M_j M_\alpha g^2); \qquad (1.1.14)$$

$$m_\alpha v_\alpha'^2 + m_j v_j'^2 = m_0 (G^2 + M_j M_\alpha g'^2), \qquad (1.1.15)$$

Fig. 1

where G, g, g' represent values of the vectors $\vec{G}$, $\vec{g}_{\alpha j}$, $\vec{g}'_{\alpha j}$. From (1.1.14) and (1.1.15) it follows that $g = g'$.

The geometry of the collision is represented in Figure 1. Let us examine the movement of molecule m_j relative to the center A of molecule m_α. Thus, in Figure 1 a coordinate system moving along with m_α is studied. In this coordinate system m_j represents a curve lying in plane PON. The plane (perpendicular to line OP) and line $AP' \| OP$ are drawn through point A. Since the force field of molecule m_α is spherically symmetrical, the lines AP', OP and ON lie in a single plane. It is easy to see that the collision is completely determined if in addition to the relative velocity $\vec{g}_{j\alpha}$ two geometrical parameters are given: the impact parameter b and the angle ε between the line of intersection of planes Z and Q and a randomly chosen direction in plane Z. Let us introduce the unit vector $\vec{k}$ as is shown in Figure 1. Let us note that the center line OA (joining the centers of the molecules at the moment of the greatest convergence) is the bisector of the angle PON. Then the value and the direction of $\vec{g}'_{j\alpha}$ are entirely determined by the vectors k and $\vec{g}_{j\alpha}$:

$$\vec{g}_{j\alpha} - \vec{g}'_{j\alpha} = 2(\vec{g}_{j\alpha} \cdot \vec{k})\vec{k}. \qquad (1.1.16)$$

Using (1.1.16), from (1.1.12) and (1.1.13) we obtain:

$$\vec{v}'_\alpha - \vec{v}_\alpha = 2M_j(\vec{g}_{j\alpha} \cdot \vec{k})\vec{k} = -2M_j(\vec{g}'_{j\alpha} \cdot \vec{k})\vec{k}; \qquad (1.1.17)$$

$$\vec{v}'_j - \vec{v}_j = -2M_\alpha(\vec{g}_{j\alpha} \cdot \vec{k})\vec{k} = 2M_\alpha(\vec{g}'_{j\alpha} \cdot \vec{k})\vec{k}. \qquad (1.1.18)$$

Let us find the number of particles expelled during time dt from a group of α-molecules per volume element $\vec{r}, d\vec{r}$ with velocities in the range $\vec{v}_\alpha, d\vec{v}_\alpha$ as a result of collisions with j-type molecules. Let us examine the movement of center B of a j-type molecule relative to center A of an α-type molecule. Let the velocity of mole-

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cule B be in the range $\vec{v}_j, d\vec{v}_j$ and the geometrical parameters of the collision be in the range $\varepsilon, d\varepsilon; b, db$. Then for a collision of this type to occur during the time dt molecule B must be in an elementary cylinder with a base area $bdbd\varepsilon$ and a height $g_{j\alpha}dt$ (see Fig. 1). It is obvious that such a cylinder represents each α-molecule of the first group, and if $db, d\varepsilon, d\vec{v}_\alpha$ are small enough we may assume that the volumes of these cylinders do not overlap. Thus, the entire volume of these cylinders is

$$dc = f_\alpha g_{j\alpha} b\,db\,d\varepsilon\,d\vec{v}_\alpha\,d\vec{r}\,dt. \tag{1.1.19}$$

The total number of j-molecules studied in this volume is:

$$f_j\,d\vec{v}_j\,dc = g_{j\alpha} f_\alpha f_j\,b\,db\,d\varepsilon\,d\vec{r}\,dt\,d\vec{v}_\alpha\,d\vec{v}_j. \tag{1.1.20}$$

Let $\sigma_{\alpha j}$ be the probability of an elastic collision of α- and j-type molecules. Then the number of elastic collisions of α- and j-molecules is $f_j \sigma_{\alpha j}\,d\vec{v}_j\,dc$. The entire number of collisions and the total number $\dfrac{\partial_e f^{(-)}}{\partial t}\,d\vec{v}_\alpha\,d\vec{r}\,dt$ of α-type molecules which leave the first group as a result of elastic collisions is found by integrating over all possible values of b, ε, $\vec{v}_j$ and by summing of all types of molecules:

$$\frac{\partial_e f_\alpha^{(-)}}{\partial t}\,d\vec{v}_\alpha\,d\vec{r}\,dt = d\vec{v}_\alpha\,d\vec{r}\,dt\sum_j \iiint f_\alpha f_j\,g_{j\alpha}\sigma_{\alpha j}\,b\,db\,d\varepsilon\,d\vec{v}_j. \tag{1.1.21}$$

Let us find the number of α-molecules which have velocities $\vec{v}_\alpha, d\vec{v}_\alpha$ as a result of collisions per volume element $\vec{r}, d\vec{r}$. Such collisions are called inverse collisions.

Repeating the considerations given above, we can show that[3]

$$\frac{\partial_e f_\alpha^{(+)}}{\partial t}\,d\vec{v}_\alpha\,dr\,dt = d\vec{v}'_\alpha\,d\vec{r}\,dt\sum_j \iiint f'_\alpha f'_j\,g'_{j\alpha}\sigma_{\alpha j}\,b'\,db'\,d\varepsilon\,d\vec{v}'_j, \tag{1.1.22}$$

where

$$f'_\alpha = f'_\alpha(\vec{r}, \vec{v}_\alpha^{\,\mathrm{inv}}, t), \quad f'_j = f'_j(\vec{r}, \vec{v}_j^{\,\mathrm{inv}}, t). \tag{1.1.23}$$

We can easily show that the velocities $\vec{v}_\alpha^{\,\mathrm{inv}}$, $\vec{v}_j^{\,\mathrm{inv}}$ which are the initial velocities of molecules in inverse collisions are equal to the final velocities of molecules in direct collisions. In fact, on the basis of analogy with (1.1.17) and (1.1.18) we can write:

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[3] It is natural to assume that the probability of an elastic collision depends on the modulus of relative velocity of the colliding molecules. Since $g = g'$, $\sigma_{\alpha j} = \sigma'_{\alpha j}$

$$\vec{v}_{\alpha}^{\,\cdot\,\text{inv}} - \vec{v}_{\alpha}^{\,\cdot\,\text{inv}} = -2M_j(\vec{g}_{j\alpha}^{\,\prime\,\text{inv}} \cdot \vec{k}^{\,\text{inv}})\vec{k}^{\,\text{inv}};$$

(1.1.24)

$$\vec{v}_{j}^{\,\prime\,\text{inv}} - \vec{v}_{j}^{\,\text{inv}} = 2M_{\alpha}(\vec{g}_{j\alpha}^{\,\prime\,\text{inv}} \cdot \vec{k}^{\,\text{inv}})\vec{k}^{\,\text{inv}}.$$

(1.1.25)

But, as we can easily see $\vec{k}^{\text{inv}} = -\vec{k}$ and $\vec{g}_{j\alpha}^{\,\prime\,\text{inv}} = \vec{g}_{j\alpha}, \vec{v}_{\alpha}^{\,\prime\,\text{inv}} = \vec{v}_{\alpha}, \vec{v}_{j}^{\,\prime\,\text{inv}} = \vec{v}_{j}$ conventionally. Then

$$\vec{v}_{\alpha} - \vec{v}_{\alpha}^{\,\text{inv}} = -2M_j(\vec{g}_{j\alpha} \cdot \vec{k})\vec{k};$$

(1.1.26)

$$\vec{v}_{j} - \vec{v}_{j}^{\,\text{inv}} = 2M_{\alpha}(\vec{g}_{j\alpha} \cdot \vec{k})\vec{k}.$$

(1.1.27)

Hence, it follows that $\vec{v}_{\alpha}^{\,\text{inv}} = \vec{v}_{\alpha}', \vec{v}_{j}^{\,\text{inv}} = \vec{v}_{j}'$. Let us show that

$$d\vec{v}_{\alpha}d\vec{v}_{j} = d\vec{v}_{\alpha}'d\vec{v}_{j}'.$$

(1.1.28)

In fact, from Jacobian theory we know that

$$d\vec{v}_{\alpha}'d\vec{v}_{j}' = |I|d\vec{v}_{\alpha}d\vec{v}_{j}; \quad d\vec{v}_{\alpha}d\vec{v}_{j} = |I'|d\vec{v}_{\alpha}'d\vec{v}_{j}'; \quad I \cdot I' = 1.$$

(1.1.29)

But, as follows from (1.1.17) - (1.1.18) $\vec{v}_{\alpha}', \vec{v}_{j}'$ are expressed linearly by $\vec{v}_{\alpha}, \vec{v}_{j}$. Making the pertinent differentiations in calculating the Jacobians and considering that, in calculating the partial derivatives, $\vec{k}$ is assumed to be a constant we can easily see that $I = I'$, whence follows (1.1.28). Considering, also, that $g_{j\alpha}' = g_{j\alpha}$ and $b' = b$ we obtain finally:

$$\frac{\partial_e f_{\alpha}}{\partial t} = \sum_{j=1}^{\mu} \iiint \sigma_{\alpha j}(f_{\alpha}'f_{j}' - f_{\alpha}f_{j})g_{\alpha j}bdbd\varepsilon d\vec{v}_{j}.$$

(1.1.30)

Thus, the Boltzmann equation which takes into account the chemical reactions in a μ-component gas mixture is written in the form

$$\frac{\partial f_{\alpha}}{\partial t} + \left(\vec{v}_{\alpha} \cdot \frac{\partial f_{\alpha}}{\partial \vec{r}}\right) + \vec{F}_{\alpha} \cdot \frac{\partial f_{\alpha}}{\partial \vec{v}_{\alpha}} = \sum_{j=1}^{\mu} \iiint (f_{\alpha}'f_{j}' - f_{\alpha}f_{j}) \times$$
$$\times g_{\alpha j}\sigma_{\alpha j}bdbd\varepsilon d\vec{v}_{j} + K_{\alpha} \quad (\alpha = 1, \ldots, \mu).$$

(1.1.31)

This derivation of the integral-differential Boltzmann equation yields a clear physical interpretation of the terms in the equation. It may be obtained in a stricter fashion from the Liouville theorem (see [2]) where kinetic equations for multiparticle distribution functions are studied.

2. The Transfer of Molecular Characteristics

Let $\vec{v}_{\alpha}$ be the velocity of a molecule of the α-component in a fixed coordinate system. Then the mean velocity of α-component

molecules is determined by the equation

$$\vec{\bar{v}}_\alpha = \frac{1}{n_\alpha} \int \vec{v}_\alpha f_\alpha (\vec{r}, \vec{v}_\alpha, t) d\vec{v}_\alpha.$$ (1.2.1)

The mean mass velocity $\vec{v}_0$ of the gas mixture is

$$\vec{\bar{v}}_0 = \frac{1}{\rho} \overset{\mu}{\underset{\alpha=1}{\Sigma}} n_\alpha m_\alpha \vec{\bar{v}}_\alpha.$$ (1.2.2)

Thus, by definition the mean mass velocity $\vec{v}_0$ is equal to the velocity at which a unit volume mass of gas must move for the impulse of this volume to be equal to the impulse of the mixture.

The heat velocity $\vec{V}_\alpha$ of a molecule is the molecular velocity relative to the coordinate system which moves at a mean mass velocity, i.e.,

$$\vec{V}_\alpha = \vec{v}_\alpha - \vec{v}_0.$$ (1.2.3)

The diffusion velocity is the mean molecular velocity of the α-component relative to the coordinate system moving at a mean mass velocity [4]:

$$\vec{\bar{V}}_\alpha = \vec{\bar{v}}_\alpha - \vec{v}_0,$$ (1.2.4)

i.e., $\vec{\bar{V}}_\alpha$ is the mean heat velocity of the α-molecules. Then the diffusion current of the α-component is

$$\vec{j}_\alpha = m_\alpha n_\alpha \vec{\bar{V}}_\alpha, \quad \alpha = 1, \ldots, \mu.$$ (1.2.5)

Summing (1.2.5) over α from 1 to μ we obtain

$$\overset{\mu}{\underset{\alpha=1}{\Sigma}} \vec{j}_\alpha = \overset{\mu}{\underset{\alpha=1}{\Sigma}} m_\alpha n_\alpha \vec{\bar{V}}_\alpha = \overset{\mu}{\underset{\alpha=1}{\Sigma}} m_\alpha n_\alpha (\vec{\bar{v}}_\alpha - \vec{v}_0) = 0.$$ 1.2.6)

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[4]Generally if $\Psi_\alpha (\vec{v}_\alpha, \vec{r}, t)$ is a random scalar vector or tensor function the mean value of $\Psi_\alpha (\vec{v}_\alpha, \vec{r}, t)$ is designated by $\overline{\Psi}_\alpha$ and determined by the equation

$$\overline{\Psi}_\alpha (\vec{r}, t) = \frac{1}{n_\alpha} \int \Psi_\alpha (\vec{v}_\alpha, \vec{r}, t) f_\alpha (\vec{v}_\alpha, \vec{r}, t) d\vec{v}_\alpha.$$ (1.2.7)

If $\Psi_\alpha (\vec{v}_\alpha, \vec{r}, t) = 1$, $\overline{\Psi}_\alpha = 1$, since obviously

$$n_\alpha = \int f_\alpha (\vec{v}_\alpha, \vec{r}, t) d\vec{v}_\alpha.$$ (1.2.8)

If $\overline{\Psi}_\alpha = \vec{v}_\alpha$, then (1.2.7) coincides with (1.2.1) which gives a definition of the mean velocity of the α-molecules; with $\Psi_\alpha = \vec{V}_\alpha$, (1.2.4) follows from (1.2.7), etc.

In the gas let us study the elementary surface ds which moves at a mean mass velocity $\vec{v}_0$ relative to the fixed coordinate system (Fig. 2), and let us introduce for ds the positive direction of the normal $\vec{n}$. Let us find the number of α-component molecules which intersect ds in the positive direction $\vec{n}$ during the time dt.
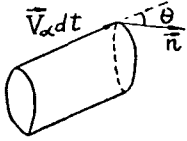
Since the characteristic velocity of α-molecules relative to ds is $\vec{V}_\alpha$, all the molecules that are initially found in the volume $d\vec{r} = V_\alpha dt ds \cos\theta$, intersect ds during the time dt. The number of these molecules is $f_\alpha(\vec{r},\vec{v},t)d\vec{V}_\alpha V_\alpha \cos\theta\, dtds$. A transfer of mass, impulse and energy occurs as a result of the current of α-molecules through ds.

Fig. 2

Any functions of $\Psi_\alpha(\vec{v}_\alpha,\vec{r},t)$ of this kind are termed molecular criteria. Thus, the current $d\Gamma_n^{(+)\Psi_\alpha}$ of the scalar molecular sign Ψ_α in the direction $\vec{n}$ is given by the equation

$$d\Gamma_n^{(+)\psi_\alpha} = \psi_\alpha(\vec{r},\vec{v}_\alpha,t)f_\alpha(\vec{r},\vec{v}_\alpha,t)V_\alpha\cos\theta\, d\vec{V}_\alpha dt ds. \qquad (1.2.9)$$

If $\vec{\Psi}_\alpha(\vec{r},\vec{v}_\alpha,t)$ is a vector function (e.g. impulse), it is convenient to study the transfer of scalar components of the molecular criterion $\vec{\Psi}_\alpha$. We obtain the current $\Gamma_n^{(+)\Psi_\alpha}$ by integrating over all high-speed groups for which $V_{\alpha n} > 0$ ($V_{\alpha n}$ is the projection of the velocity $\vec{V}_\alpha$ for the direction $\vec{n}$).

$$\Gamma_n^{(+)\psi_\alpha} = ds\, dt \int_{V_{\alpha n}>0} \psi_\alpha f_\alpha V_{\alpha n}\, d\vec{V}_\alpha. \qquad (1.2.10)$$

In an entirely analogous fashion the current Ψ_α in the negative direction of the normal $\vec{n}$ is given by the expression

$$\Gamma_n^{(-)\psi_\alpha} = -ds\, dt \int_{V_{\alpha n}<0} \psi_\alpha f_\alpha V_{\alpha n}\, d\vec{V}_\alpha. \qquad (1.2.11)$$

The minus sign was placed in (1.2.11) so that the expression for the volume element $d\vec{r}$ will be positive. The entire current Ψ_α in the positive direction $\vec{n}$ is $\Gamma_n^{\Psi_\alpha}$:

$$\Gamma_n^{\psi_\alpha} = \Gamma_n^{(+)\psi_\alpha} - \Gamma_n^{(-)\psi_\alpha} = ds\, dt \int \psi_\alpha f_\alpha V_{\alpha n}\, d\vec{V}_\alpha, \qquad (1.2.12)$$

where the integration is performed over all the values of $\vec{V}_\alpha$. The specific current of the sign Ψ_α is

$$\gamma_n^{\psi_\alpha} = \int \psi_\alpha f_\alpha V_{\alpha n}\, d\vec{V}_\alpha. \qquad (1.2.13)$$

Let us study the mass, impulse and energy transfer in the gas.

1. Let $\Psi_\alpha = m_\alpha$. Then the equation for the projection of the vector of the mass diffusion current for the direction $\vec{n}$ follows from (1.2.13):

$$J_{\alpha n} = m_\alpha \int f_\alpha V_{\alpha n} \, d\vec{V}_\alpha = m_\alpha n_\alpha \overline{V}_{\alpha n}. \qquad (1.2.14)$$

2. If $\Psi_\alpha = m_\alpha V_{\alpha i}$ ($i = 1,2,3$) then (1.2.13) determines the transfer of the i-component of the impulse in the direction $\vec{n}$. Let the direction of the vector $\vec{n}$ alternately coincide with unit vectors in the positive direction of the coordinate axes. Then, it is obvious that the impulse transfer of the α-component is determined by a symmetrical tensor of second rank.

$$P_\alpha = m_\alpha n_\alpha \overline{\vec{V}_\alpha \vec{V}_\alpha}, \qquad (1.2.15)$$

where $\overline{\vec{V}_\alpha \vec{V}_\alpha}$ is a dyad with nine components,

$$P_\alpha = \left\{ \begin{array}{ccc} \rho_\alpha \overline{V_{\alpha 1} V_{\alpha 1}}, & \rho_\alpha \overline{V_{\alpha 1} V_{\alpha 2}}, & \rho_\alpha \overline{V_{\alpha 1}, V_{\alpha 3}} \\ \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\ \rho_\alpha \overline{V_{\alpha 3} V_{\alpha 1}}, & \rho_\alpha \overline{V_{\alpha 3} V_{\alpha 2}}, & \rho_\alpha \overline{V_{\alpha 3} V_{\alpha 3}} \end{array} \right\}$$

The sum of the tensors of the partial pressures yields a tensor of the gas mixture pressures

$$P = \sum_\alpha m_\alpha n_\alpha \overline{\vec{V}_\alpha \vec{V}_\alpha}. \qquad (1.2.16)$$

The pressure vector $\vec{p}_n$ per surface element can not coincide with the normal to this surface. The normal pressure component per surface element situated randomly in a gas is primarily positive:

$$\vec{p}_n \cdot \vec{n} = \sum_\alpha \rho_\alpha \overline{\vec{V}_\alpha V_{\alpha n}} \cdot \vec{n} = \sum_\alpha \rho_\alpha \overline{V_{\alpha n}^2}. \qquad (1.2.17)$$

By definition the average of normal pressures on any three mutually orthogonal planes yields a hydrostatic pressure in the gas:

$$p = \frac{1}{3} \sum_\alpha \rho_\alpha \overline{V_{\alpha n}^2}. \qquad (1.2.18)$$

3. Let $\Psi \quad \frac{1}{2} m_\alpha \vec{V}_\alpha^2$. Then (1.2.13) determines the projection for the direction $\vec{n}$ of the kinetic energy current vector through the surface element which is moving at a mean mass velocity

$$q_n = \sum_\alpha q_{\alpha n} = \sum_\alpha \frac{1}{2} m_\alpha n_\alpha \overline{\vec{V}_\alpha^2 V_{\alpha n}}. \qquad (1.2.19)$$

Let us study the amount of molecular kinetic energy per unit
volume at the moment of time t:

$$E_{kin} = \sum_\alpha \int \frac{1}{2} m_\alpha \vec{v}_\alpha^2 f_\alpha d\vec{v}_\alpha = \sum_\alpha \frac{1}{2} m_\alpha n_\alpha \overline{\vec{v}_\alpha^2} , \qquad (1.2.20)$$

but $\vec{v}_\alpha = \vec{v}_0 + \vec{V}_\alpha$; using (1.2.6) we obtain

$$E_{kin} = \sum_\alpha \frac{1}{2} m_\alpha n_\alpha \vec{v}_0^2 + \sum_\alpha \frac{1}{2} m_\alpha n_\alpha \overline{\vec{V}_\alpha^2} = \frac{\rho \vec{v}_0^2}{2} + \sum_\alpha \frac{\rho_\alpha \overline{\vec{V}_\alpha^2}}{2} . \qquad (1.2.21)$$

Thus, the kinetic energy per volume element of the gas mixture
is accumulated from the energy of the visible mass movement of
the gas (E_{macr}) and from the energy of the chaotic molecular move-
ment (E_{micr}), with

$$(E_{micr}/E_{macr}) \sim (\overline{\vec{V}^2}/\vec{v}_0^2). \qquad (1.2.22)$$

Let us estimate the order of magnitude of this ratio. We know from
experiment that, for example, for nitrogen at a temperature $T = 273.16°K$ and pressure $p = 760$ mm Hg the density $\rho = 1.25 \cdot 10^{-3} g/cm^3$
Then from (1.2.18) $\overline{V^2} \sim 2.43 \cdot 10^9$ cm$^2 \cdot$sec^{-2} and for the mean mass
velocity $v_0 \sim 1$ cm/sec, $E_{micr}/E_{macr} \sim 2.43 \cdot 10^5$. Under these con-
ditions almost all the kinetic energy of the molecules consists of
the energy of their chaotic movement. However, in addition to
translational movement energy molecules can possess vibration
energy, rotation energy, etc. During chemical reactions we must
take into account the molecular potential energy which converts to
kinetic energy during interatomic bond breaking in the molecule.
All these forms of energy together with the energy of the chaotic
movement of the molecules are identified in the kinetic theory of
gases with thermal energy E_{therm}. Thus when molecules are studied

as point centers of force, $E_{therm} = E_{micr} = \sum_\alpha \frac{\rho_\alpha}{2} \overline{V^2_\alpha}$. The tempera-
ture of the translational movement is determined by the equation

$$\frac{1}{2} m_\alpha \overline{\vec{V}_\alpha^2} = \frac{3}{2} kT, \qquad (1.2.23)$$

where k is the Boltzmann constant independent of the kind of gas
($k = 1.38 \cdot 10^{-16}$ erg/deg).

Using (1.2.18) we find

$$p_\alpha = n_\alpha kT, \qquad (1.2.24)$$
$$p = kT \sum_\alpha n_\alpha. \qquad (1.2.25)$$

Let the mass w_α of the gas α be found in the volume V at a pressure
p and a temperature T. Then from (1.2.24)

$$pV = k \frac{w_\alpha}{m_\alpha} T. \qquad (1.2.26)$$

From (1.2.26) it is evident that the number of gas molecules in the volume V at the same pressure p and temperature T is independent of the kind of gas. This conclusion is Avogadro's law. On the other hand we may assume that Avogadro's law was extablished experimentally and that, therefore, it has been established that the constant k and the mean kinetic energy of the molecules are independent of the kind of gas. This conclusion has been obtained by other means in statistical physics. The simplest study is in [3]. Historically the molecular weight of a gas is determined by the equation [5]

$$M_\alpha = 16 m_\alpha / m_0 \quad \text{g/mole} \qquad (1.2.27)$$

where m_α, m_0, are respectively the masses of the molecules of the gas α and an oxygen atom. It is obvious that the number of molecules $N = M_\alpha / m_\alpha = 16 / m_0$ is independent of the kind of gas. The number $N = 6.023 \cdot 10^{23}$ is usually called Avogadro's number.

Let heat $d\tilde{Q}_\alpha$ be applied to the mass of gas w_α as a result of which the gas heats to a temperature $T + dT$. This heat is required for the completion of the mechanical work $p_\alpha dV$ and an increase in the thermal energy. Then

$$d\tilde{Q}_\alpha = p_\alpha dV + \frac{d E_\alpha}{m_\alpha} w_\alpha , \qquad (1.2.28)$$

where $\overline{E}_\alpha$ is the thermal energy of an α-type molecule. For a process occurring at a constant volume we obtain

$$d\tilde{Q}_\alpha = d \overline{E}_\alpha w_\alpha / m_\alpha \qquad (1.2.29)$$

and at a constant pressure

$$d\tilde{Q}_\alpha = (k dT + d \overline{E}_\alpha) w_\alpha / m_\alpha. \qquad (1.2.30)$$

By definition the heat capacity of a unit mass of the gas α at constant volume is

$$C_{v\alpha} = \frac{1}{w_\alpha} \left(\frac{d \tilde{Q}_\alpha}{d T} \right)_V = \frac{1}{m_\alpha} \left(\frac{d \overline{E}_\alpha}{d T} \right)_V \quad \text{cal/g-deg} \qquad (1.2.31)$$

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[5] Here and below M_α signifies the molecular weight of the α-component.

and at a constant pressure it is

right

$$C_{p\alpha} = \frac{1}{w_\alpha}\left(\frac{d\tilde{Q}_\alpha}{dT}\right)_p = \frac{1}{m_\alpha}\left[k + \left(\frac{d\bar{E}_\alpha}{dT}\right)_p\right].$$

right

(1.2.32)

If we assume that molecular thermal energy depends only on temperature and not on pressure and volume, then from (1.2.31) and (1.2.32) it follows that

$$C_{p\alpha} - C_{v\alpha} = k/m_\alpha.$$

(1.2.33)

As experiments show, the difference $C_{p\alpha} - C_{v\alpha}$ is actually constant for a sufficiently rarefied gas. If molecular thermal energy consists only of chaotic movement energy then using (1.2.23) we obtain

$$C_{v\alpha} = 3k/2m_\alpha; \quad C_{p\alpha} = 5k/2m_\alpha.$$

(1.2.34)

In this case, the heat capacity does not depend on temperature. In fact, the internal degrees of molecular freedom substantially influence the heat capacity which is dependent on temperature. Table 1 illustrates this (c_p, in Cal/mole·deg)

TABLE 1

c_{pi}	Temperature $^\circ K$					
	1000	3000	5000	7000	9000	11000
$c_{p,C}$	4,970	5,170	5,470	5,588	5,810	7,247
$c_{p,CO}$	7,930	8,895	9,100	9,362	10,11	12,16
c_{p,CO_2}	12,96	14,88	15,32	14,84	14,87	14,88
$c_{p,O}$	4,997	5,002	5,208	5,410	5,513	5,569
c_{p,O_2}	8,333	9,552	10,20	10,34	9,882	9,098

By definition the enthalpy of α-type molecules is

$$h_\alpha = \frac{1}{m_\alpha}(\bar{E}_\alpha + kT),$$

(1.2.35)

while the enthalpy of the mixture

$$h = \sum_\alpha \frac{\rho_\alpha}{\rho} h_\alpha = \sum_\alpha c_\alpha h_\alpha,$$

(1.2.36)

right

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where c_α is the mass concentration of the α-component, $c_\alpha = \rho_\alpha/\rho$.
From (1.2.32) it follows that [6]

$$c_{p\alpha} = (\partial h_\alpha/\partial T)_p.$$ (1.2.37)

As is easily seen, (1.2.28) is the first law of thermodynamics. In thermochemistry in contrast to thermodynamics it is justifiable to consider the heat which is given off in the system during the flow of chemical reactions. If we designate the thermal reaction effects at a constant volume and pressure by Q_v and Q_p, then

$$Q_v = -\tilde{Q}_v;$$ (1.2.38)

$$Q_p = -\tilde{Q}_p.$$ (1.2.39)

If a system consisting of α(α = 1,...,μ) components transferred with a constant volume from state 1 (overall internal energy E_1) to state 2 (E_2) as a result of chemical reactions, then

$$Q_v = E_1 - E_2.$$ (1.2.40)

For the process at a constant pressure, using (1.2.35) and (1.2.36) we obtain

$$Q_p = (E_1 + pV_1) - (E_2 - pV_2) = w(h_1 - h_2),$$ (1.2.41)

where $w = \sum_\alpha w_\alpha$.

Thus, the elementary thermal effect in the isochoric and isobaric cases is a full differential but Q_v and Q_p do not depend on the transfer path of the system from one state to the other. This assertion is known by the name Hess law. From (1.2.40) and (1.2.41) there follows a connection between the respective thermal effects:

$$Q_v = Q_p + p\Delta V.$$ (1.2.42)

According to Hess law it follows that if identical products are formed from two different systems as a result of different processes, then the difference in the thermal effects of these processes is equal to the heat transfer from the first system to the second. Thus, the thermal reaction effect is equal to the algebraic sum of the heats of formation of reagents from simple materials. The standard heat of formation of a given material is defined as the

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[6] By analogy with (1.2.36) let us determine the heat capacity of the mixture by the equation $c_p = \sum_\alpha c_\alpha c_{p\alpha}$.

heat required to obtain one mole of material during formation from elements in their standard state [generally 298.16°K (25°C) and zero pressure]. For ideal gases the heat of formation determined in this way is equal to the heat of formation at a pressure of 1 atm. For the majority of real gases there is a very small difference between the heats of formation at zero pressure and at a pressure of 1 atm, the greatest difference being several calories. The standard state for each element is a state in which it is most stable at 25°C and $p = 1$ atm, e.g., H_2, O_2, N_2 for hydrogen, oxygen and nitrogen, a liquid state for Hg and crystalline graphite for C, etc.

Sometimes it is convenient to look at the formation enthalpies at 0°K (see Table 2).

TABLE 2

α-component.	Formation enthalpy at 0°K, kCal/mole, h_α^0
C	264
CO	66.77
CO_2	0
O	58.97
O_2	0
C^+	623.8
CO^+	390.4
O^+	372.9
O_2^+	282.4

3. Transfer Equations and Summational Invariants

Let us introduce a general Enskog transfer equation of the molecular criterion Ψ_2. Let us multiply the Boltzmann equation by Ψ_2 and integrate over all the values of $\vec{v}_\alpha$. As a result we obtain

$$\int \psi_\alpha \left(\frac{\partial f_\alpha}{\partial t} + \vec{v}_\alpha \cdot \frac{\partial f_\alpha}{\partial \vec{r}} + \vec{F}_\alpha \cdot \frac{\partial f_\alpha}{\partial \vec{v}_\alpha} \right) d\vec{v}_\alpha = \sum_{j=1}^{\mu} \iiiint \psi_\alpha (f_\alpha' f_j' - f_\alpha f_j) \times$$

$$\times \sigma_{\alpha j} g_{\alpha j} b\, db\, d\varepsilon\, d\vec{v}_\alpha\, d\vec{v}_j + \int \psi_\alpha K_\alpha d\vec{v}_\alpha.$$

(1.3.1)

Using the expressions for the mean values we obtain

$$\int \psi_\alpha \frac{\partial f_\alpha}{\partial t} d\vec{v}_\alpha = \frac{\partial}{\partial t} \int \psi_\alpha f_\alpha d\vec{v}_\alpha - \int f_\alpha \frac{\partial \psi_\alpha}{\partial t} d\vec{v}_\alpha = \frac{\partial n_\alpha \overline{\psi}_\alpha}{\partial t} - n_\alpha \overline{\frac{\partial \psi_\alpha}{\partial t}}; \qquad (1.3.2)$$

$$\int \psi_\alpha \vec{v}_\alpha \cdot \frac{\partial f_\alpha}{\partial \vec{r}} d\vec{v}_\alpha = \frac{\partial}{\partial \vec{r}} \cdot \int \psi_\alpha \vec{v}_\alpha f_\alpha d\vec{v}_\alpha - \int f_\alpha \vec{v}_\alpha \cdot \frac{\partial \psi_\alpha}{\partial \vec{r}} d\vec{v}_\alpha =$$

$$= \frac{\partial}{\partial \vec{r}} \cdot (n_\alpha \overline{\psi_\alpha \vec{v}_\alpha}) - n_\alpha \overline{\vec{v}_\alpha \cdot \frac{\partial \psi_\alpha}{\partial \vec{r}}}. \qquad (1.3.3)$$

In differentiating we must remember that $\vec{r}, \vec{v}_\alpha$ are independent variables. Since the forces $\vec{F}_\alpha$ are assumed independent of the molecular velocities and $\psi_\alpha f_\alpha \to 0$ with $\vec{v}_\alpha \to \infty$ then

$$\int \psi_\alpha F_{\alpha 1} \frac{\partial f_\alpha}{\partial v_{\alpha 1}} d\vec{v}_\alpha = F_{\alpha 1} \int\int [\psi_\alpha f_\alpha]_{v_{\alpha 1}=-\infty}^{v_{\alpha 1}=+\infty} dv_{\alpha 2} dv_{\alpha 3} -$$

$$- F_{\alpha 1} \int f_\alpha \frac{\partial \psi_\alpha}{\partial v_{\alpha 1}} d\vec{v}_\alpha = - n_\alpha F_{\alpha 1} \overline{\frac{\partial \psi_\alpha}{\partial v_{\alpha 1}}}. \qquad (1.3.4)$$

Thus, the Enskog equation:

$$\frac{\partial n_\alpha \overline{\psi}_\alpha}{\partial t} + \frac{\partial}{\partial \vec{r}} \cdot (n_\alpha \overline{\psi_\alpha \vec{v}_\alpha}) - n_\alpha \left[\overline{\frac{\partial \psi_\alpha}{\partial t}} + \overline{\vec{v}_\alpha \cdot \frac{\partial \psi_\alpha}{\partial \vec{r}}} + \overline{\vec{F}_\alpha \cdot \frac{\partial \psi_\alpha}{\partial \vec{v}_\alpha}} \right] = \qquad (1.3.5)$$

$$= \sum_j \int\int\int\int \psi_\alpha (f'_\alpha f'_j - f_\alpha f_j) \sigma_{\alpha j} g_{\alpha j} b\, db\, d\varepsilon\, d\vec{v}_\alpha d\vec{v}_j + \int K_\alpha \psi_\alpha d\vec{v}_\alpha.$$

Equation (1.3.5) is an integral-differential equation and, generally speaking, it is no simpler than the Boltzman equation from which it was obtained. However, for so-called summational invariants the integral term $\partial e f_\alpha / \partial t$ is changed to zero and equation (1.3.5) is substantially simplified [7]. The integral $\int K_\alpha d\vec{v}_\alpha$ is the number of particles of the α-component which are formed per unit volume per unit of time. Then, obviously:

$$\int K_\alpha m_\alpha d\vec{v}_\alpha = R_\alpha, \qquad (1.3.6)$$

where R_α is the mass velocity of the formation of the α-component.

$$\sum_\alpha \int K_\alpha m_\alpha d\vec{v}_\alpha = \sum_\alpha R_\alpha = 0, \qquad (1.3.7)$$

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[7] The values which satisfy the condition $\psi_\alpha + \psi_j = \psi'_\alpha + \psi'_j$ are called additive collision invariants.

since the mass velocity of the formation of the material as a
result of chemical reactions is zero (we assume that nuclear re-
actions do not occur). Let us write the condition for the conser-
vation of momentum during chemical conversions:

$$\sum_\alpha \int K_\alpha m_\alpha \vec{V}_\alpha d\vec{v}_\alpha = 0. \qquad (1.3.8)$$

Finally, the condition for the conservation of energy is:

$$\sum_\alpha \int K_\alpha \left(\frac{m_\alpha \vec{V}_\alpha^2}{2} + u_\alpha^{(int)} \right) d\vec{v}_\alpha = 0. \qquad (1.3.9)$$

It is easily shown that the first integral on the right-hand side
for collison invariants (m_α, $m_\alpha \vec{V}_\alpha$ $\frac{m_\alpha \vec{V}_\alpha^2}{2} + u_\alpha^{(int)}$ changes to zero.
In fact,

$$\iiint m_\alpha (f_\alpha' f_j' - f_\alpha f_j) \sigma_{\alpha j}\, g_{\alpha j}\, b\, db\, d\varepsilon\, d\vec{v}_\alpha\, d\vec{v}_j =$$

$$= \iiint m_\alpha' (f_\alpha f_j - f_\alpha' f_j') \sigma_{\alpha j}\, g_{\alpha j}'\, b'\, db'\, d\varepsilon\, d\vec{v}_\alpha'\, d\vec{v}_j'. \qquad (1.3.10)$$

However, during elastic collisions $m_\alpha = m_\alpha'$, $b = b'$, $d\vec{v}_\alpha d\vec{v}_j = d\vec{v}_\alpha' d\vec{v}_j'$,
$g_{\alpha j} = g_{\alpha j}'$ [see (1.1.15), (1.1.28)]. From (1.3.10) it follows that

$$\iiint m_\alpha (f_\alpha' f_j' - f_\alpha f_j) \sigma_{\alpha j}\, g_{\alpha j}\, b\, db\, d\varepsilon\, d\vec{v}_\alpha\, d\vec{v}_j = 0. \qquad (1.3.11)$$

The conversion of this integral into zero for other collision in-
variants is proved analogously [4]. Thus, by successively sub-
stituting collision invariants into (1.3.5) we obtain an equation
of continuity for the components

$$\frac{\partial n_\alpha m_\alpha}{\partial t} + \frac{\partial}{\partial \vec{r}} \cdot (m_\alpha n_\alpha \vec{v}_\alpha) = R_\alpha, \qquad (1.3.12)$$

an equation of gas motion

$$\sum_\alpha \left[\frac{\overline{\partial m_\alpha n_\alpha \vec{V}_\alpha}}{\partial t} + \frac{\partial}{\partial \vec{r}} \cdot m_\alpha n_\alpha \overline{\vec{v}_\alpha \vec{V}_\alpha} - n_\alpha \left(\frac{\overline{\partial m_\alpha \vec{V}_\alpha}}{\partial t} + \vec{v}_\alpha \frac{\overline{\partial m_\alpha \vec{V}_\alpha}}{\partial \vec{r}} + \vec{F}_\alpha \frac{\overline{\partial m_\alpha \vec{V}_\alpha}}{\partial \vec{v}_\alpha} \right) \right] = 0 \qquad (1.3.13)$$

and an energy equation

$$\sum_{\alpha}\left[\overline{\frac{\partial n_{\alpha}\overline{E_{\alpha}}}{\partial t}} + \frac{\partial}{\partial \vec{r}} \cdot \overline{n_{\alpha}\vec{v}_{\alpha}E_{\alpha}} - n_{\alpha}\left(\overline{\frac{\partial E_{\alpha}}{\partial t}} + \vec{v}_{\alpha} \cdot \overline{\frac{\partial E_{\alpha}}{\partial \vec{r}}} + \vec{F}_{\alpha} \cdot \overline{\frac{\partial E_{\alpha}}{\partial \vec{v}_{\alpha}}}\right)\right] = 0. \qquad (1.3.14)$$

In the next equation E_{α} is the full internal energy of the α-compo- <u>/24</u>
nent molecule:

$$E_{\alpha} = \frac{m_{\alpha}\vec{V}_{\alpha}^{2}}{2} + u_{\alpha}^{(int)}. \qquad (1.3.15)$$

Let us perform a conversion of the equations obtained.

1. Equation of continuity. If we take into account the fact
that the density of the α-component $\rho_{\alpha} = m_{\alpha}n_{\alpha}$ and we take into
account equations (1.2.4) and (1.2.5) then (1.3.12) reduces to the
form

$$\frac{\partial \rho_{\alpha}}{\partial t} + \mathrm{div}\,(\rho_{\alpha}\vec{v}_{0} + \vec{j}_{\alpha}) = R_{\alpha}. \qquad (1.3.16)$$

Summing up the equations (1.3.16) over $\alpha(\alpha = 1,\dots,\mu)$ and using
(1.2.6) and (1.3.7) we obtain an equation of continuity for the
gas mixture:

$$\frac{\partial \rho}{\partial t} + \mathrm{div}\,\rho\,\vec{v}_{0} = 0. \qquad (1.3.17)$$

2. Equation of motion. The first term of (1.3.13) is equal
to zero in virtue of (1.2.6). The second term of the equation:

$$\sum_{\alpha}\frac{\partial}{\partial \vec{r}} \cdot \overline{\rho_{\alpha}\vec{v}_{\alpha}\vec{V}_{\alpha}} = \sum_{\alpha}\frac{\partial}{\partial \vec{r}} \cdot \overline{\rho_{\alpha}\vec{V}_{\alpha}\vec{V}_{\alpha}} = \frac{\partial}{\partial \vec{r}} \cdot P = \sum_{\alpha=1}^{\mu}\sum_{i=1}^{3}\frac{\partial}{\partial x_{i}}\overline{\rho_{\alpha}V_{\alpha i}\vec{V}_{\alpha}}, \qquad (1.3.18)$$

where the tensor P is determined by (1.2.16). When converting
the other terms we must take into account the fact that $\vec{v}_{\alpha}$ and $\vec{r}$
are considered independent variables. Thus the equation of motion:

$$\frac{\partial \vec{v}_{0}}{\partial t} + \vec{v}_{0} \cdot \frac{\partial}{\partial \vec{r}}\vec{v}_{0} = -\frac{1}{\rho}\frac{\partial}{\partial \vec{r}} \cdot P + \frac{1}{\rho}\sum_{\alpha}\rho_{\alpha}\vec{F}_{\alpha}. \qquad (1.3.19)$$

3. Equation of energy. Let us introduce the thermodynamic
internal energy $\tilde{E}$ necessary for 1 g of the mixture at the moment
of time t:

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$$\tilde{E} = \frac{1}{\rho} \sum_\alpha \int E_\alpha f_\alpha \, d\vec{v}_\alpha = \frac{1}{\rho} \sum_\alpha n_\alpha \bar{E}_\alpha = \frac{1}{\rho} \left(\sum_\alpha \frac{m_\alpha n_\alpha \overline{\vec{V}_\alpha^2}}{2} + \sum_\alpha n_\alpha \bar{u}_\alpha^{(int)} \right),$$
(1.3.20)

and the heat flux [cf.(1.2.19)]:

$$\vec{q} = \sum_\alpha \frac{1}{2} m_\alpha n_\alpha \overline{\vec{V}_\alpha^2 \vec{V}_\alpha} + \sum_\alpha n_\alpha \overline{\vec{V}_\alpha u_\alpha^{(int)}}.$$
(1.3.20')

Then the equation of energy reduces to the form

$$\rho \frac{\partial \tilde{E}}{\partial t} + \rho \vec{v}_0 \cdot \frac{\partial}{\partial \vec{r}} \tilde{E} + \frac{\partial}{\partial \vec{r}} \cdot \vec{q} + P : \frac{\partial}{\partial \vec{r}} \vec{v}_0 - \sum_\alpha \rho_\alpha \vec{F}_\alpha \cdot \overline{\vec{V}_\alpha} = 0,$$
(1.3.21) <u>/25</u>

where

$$P : \frac{\partial}{\partial \vec{r}} \vec{v}_0 = \sum_\alpha \rho_\alpha \overline{\vec{V}_\alpha \vec{V}_\alpha} : \frac{\partial}{\partial \vec{r}} \vec{v}_0 = \sum_{\alpha=1}^{\mu} \sum_{i=1}^{3} \rho_\alpha \overline{\vec{V}_\alpha V_{\alpha i}} \cdot \frac{\partial \vec{v}_0}{\partial x_i}.$$
(1.3.22)

Using (1.3.20), (1.2.35) and (1.2.36) we obtain

$$\tilde{E} = h - \sum_\alpha c_\alpha p_\alpha / \rho_\alpha = h - p/\rho.$$
(1.3.23)

It is easily shown (using the equation of continuity) that the substantial derivative

$$\frac{d}{dt} \tilde{E} = \frac{dh}{dt} - \frac{1}{\rho} \frac{dp}{dt} - \frac{p}{\rho} \operatorname{div} \vec{v}_0.$$
(1.3.24)

Taking into account (1.3.24) let us convert the equation of energy to the form

$$\rho \frac{dh}{dt} = \frac{dp}{dt} + p \operatorname{div} \vec{v}_0 - P : \frac{\partial}{\partial \vec{r}} \vec{v}_0 + \sum_\alpha \rho_\alpha \vec{F}_\alpha \cdot \overline{\vec{V}_\alpha} - \frac{\partial}{\partial \vec{r}} \cdot \vec{q}.$$
(1.3.25)

Let us emphasize that the equation of energy (1.3.25) includes the entire enthalpy of the h mixture taking into account the formation enthalpies of the components. Equations (1.3.16), (1.3.17), (1.3.19) and (1.3.25) form a system of hydrodynamic equations for the reacting gas mixture. These equations include diffusion currents, heat flux $\vec{q}$ and the pressure tensor P. To obtain specific standard working formulas for these values we must solve the Boltzmann equation. Below we will present a sketch of the method (belonging to Enskog) for solving the Boltzmann equation. Phenomenological ties between the stress tensor and the deformation velocity tensor, the heat flux and the temperature gradient remain the same as in a homogeneous gas, but the coefficients of viscosity, thermal conductivity and diffusion depend on the concentrations of all the gas mixture components.

In view of the importance of hydrodynamic equations of a reacting gas mixture we will give their derivation by balance equations as is usually done in hydrodynamics. In the gas we will select a certain volume w which is moving at a mean mass velocity $\vec{v}_0$. The current of the mass of the α-component across the volume surface as a result of diffusion $\vec{j}_\alpha = m_\alpha n_\alpha \vec{V}_\alpha$. But according to (1.2.6) $\sum_\alpha \vec{j}_\alpha = 0$ therefore, in the presence of diffusion the mass of the selected volume is conserved. Let us also note that $\sum_\alpha R_\alpha = 0$, since during chemical reactions the total mass is conserved. $\underline{/26}$ Therefore,

$$\frac{d}{dt} \iiint\limits_w \rho dw = 0,$$

(1.3.26)

whence follows the equation of continuity

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \rho \vec{v}_0 = 0.$$

(1.3.27)

It is easy to obtain the equation of continuity for the α-component. To do this we will write the equation for the conservation of mass of the α-component in the volume w in integral form.

$$\frac{d}{dt} \iiint\limits_w \rho_\alpha dw = -\iint\limits_\sigma \vec{J}_\alpha \cdot \vec{n} d\sigma + \iiint\limits_w R_\alpha dw,$$

(1.3.28)

here $\vec{n}$ is the outward normal to the surface σ of the volume w. Using the Gaussian theorem let us obtain

$$\frac{\partial \rho_\alpha}{\partial t} + \operatorname{div}(\rho_\alpha \vec{v}_0 + \vec{J}_\alpha) = R_\alpha, \quad \alpha = 1, \dots, \mu.$$

(1.3.29)

Summing (1.3.29) over α we obtain, as was to be expected, the equation of continuity (1.3.27).

The rates of the formation of the R_α-components as a result of chemical reactions, generally depend on the concentrations of c_α (see Chapter 2, Section 1). Thus, equations of continuity for components which are written via mass concentrations of separate components of the mixtures are inhomogeneous as a result of the presence of homogeneous chemical reactions in the gas flow. Sometimes it is convenient to operate with homogeneous equations. With the absence of the intranuclear reactions ν, homogeneous diffusion equations for elements where ν is the number of elements in the gas mixture may be obtained from the μ equations of continuity. In fact, since no element is formed nor disappears in the chemical reactions, then

$$\sum_{\alpha=1}^{\mu} \frac{n_{\tau\alpha} M_\tau}{M_\alpha} R_\alpha = 0,$$

(1.3.30)

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since $n_{\tau\alpha}M_\tau R_\alpha/M_\alpha$ is the mass speed of the transfer of an element τ to the composition of the α-material as a result of all the chemical reactions. Here $n_{\tau\alpha}$ signifies the number of atoms of the element τ in the composition of the α-component. Thus, the equation of continuity for the elements will be

$$\frac{\partial}{\partial t}\rho\sum_\alpha\frac{n_{\tau\alpha}c_\alpha}{M_\alpha}+\text{div}\sum_\alpha\frac{n_{\tau\alpha}}{M_\alpha}(\rho c_\alpha\vec{v}_0+\vec{j}_\alpha)=0. \qquad (1.3.31)$$

V.A. Shvav [5] and Ya. V. Zel'sovich [6], in studying combustion processes, included a study of the concentration of elements for the first time. Liz used this concept for studying heat transfer with the Lewis number $L = 1$ [7].

The equation of motion for a mixture of reacting gases coincides with the Navier-Stokes equation of motion for a homogeneous compressible gas. We must emphasize only the fact that the mean mass velocity of the flow is included in an aerothermochemical equation of motion. Under normal assumptions with respect to the relationship between the stress tensor and the velocity deformation tensor we obtain

$$\rho\frac{d\vec{v}_0}{dt}=\sum_\alpha\rho_\alpha\vec{F}_\alpha-\text{grad}\,p+\sum_{i=1}^{3}\frac{\partial\vec{\tau}_{x_i}}{\partial x_i}; \qquad (1.3.32)$$

$$\left.\begin{array}{l}\tau_{x_{ii}}=2\eta\dfrac{\partial v_{0i}}{\partial x_i}+\lambda\,\text{div}\,\vec{v}_0\,,\quad i=1,2,3;\\[2mm]\tau_{x_{ij}}=\eta\left(\dfrac{\partial v_{0i}}{\partial x_j}+\dfrac{\partial v_{0j}}{\partial x_i}\right),\quad i\neq j\,,\end{array}\right\} \qquad (1.3.33)$$

here $\lambda = -2/3\eta$, and η is the viscosity of the gas mixture.

Let us look at the equation of energy for the volume w moving at a mean mass velocity.

$$\frac{d}{dt}\iiint_w\left[\rho\left(\frac{\vec{v}_0^2}{2}+\tilde{E}\right)\right]dw=\iiint_w\sum_\alpha\rho_\alpha\vec{F}_\alpha\overline{\vec{v}}_\alpha\,dw-\iint_\sigma p\,v_{0n}\,d\sigma+ \qquad (1.3.34)$$

$$+\iint_\sigma\sum_{i=1}^{3}\vec{t}_{x_i}\vec{v}_0\cos\widehat{nx_i}\,d\sigma+\iint_\sigma\varkappa\frac{\partial T}{dn}\,d\sigma-\iint_\sigma\sum_{\alpha=1}^{\mu}j_{\alpha n}h_\alpha\,d\sigma.$$

The equation of energy was written in a form similar to the first law of thermodynamics. The left-hand side of the equation of energy is the change of the kinetic and internal energy of the moving volume with respect to time. The first term of the right-hand side takes into account the work of the mass forces, the second takes into account the work of the pressure forces, the third the work of the friction forces, the fourth, the entry of the energy

into the volume as a result of thermal conductivity and the fifth as a result of diffusion. It is assumed that all the values are expressed in thermal units. But since, as we already mentioned, the mass of the volume w moving at a mean mass speed is conserved, a normal conversion is possible:

$$\frac{d}{dt}\iiint_w \rho\left[\frac{\vec{v}_0^2}{2}+\tilde{E}\right]dw = \frac{d}{dt}\iiint_M\left[\frac{\vec{v}_0^2}{2}+\tilde{E}\right]dm = \iiint_w \rho\frac{d}{dt}\left[\frac{\vec{v}_0^2}{2}+\tilde{E}\right]dw. \qquad (1.3.35)$$

Converting the integrals over the surface σ into integrals over the volume w by means of the Gaussian theorem, and taking into account the arbitrariness in the value of the volume w, we obtain

$$\rho\frac{d}{dt}\left(\frac{\vec{v}_0^2}{2}+\tilde{E}\right) = \sum_\alpha \rho_\alpha\vec{F}_\alpha\cdot\overline{\vec{v}}_\alpha - \operatorname{div}p\,\vec{v}_0 + \sum_{i=1}^{3}\frac{\partial}{\partial x_i}\vec{\tau}_{x_i}\cdot\vec{v}_0 +$$
$$+ \operatorname{div}(\varkappa\operatorname{grad}T) - \operatorname{div}\sum_\alpha \vec{j}_\alpha h_\alpha. \qquad (1.3.36)$$

Scalar multiplication of the equation of motion by $\vec{v}_0$ gives

$$\rho\vec{v}_0\cdot\frac{d\vec{v}_0}{dt} = \sum_\alpha \rho_\alpha\vec{F}_\alpha\cdot\vec{v}_0 - \vec{v}_0\operatorname{grad}p + \sum_{i=1}^{3}\vec{v}_0\frac{\partial\vec{\tau}_{x_i}}{\partial x_i}. \qquad (1.3.37)$$

Equation (1.3.36) with the help of (1.3.37) is simplified and reduced to the form

$$\rho\frac{d}{dt}\tilde{E} = \sum_{i=1}^{3}\vec{\tau}_{x_i}\cdot\frac{\partial\vec{v}_0}{\partial x_i} - p\operatorname{div}\vec{v}_0 + \operatorname{div}(\varkappa\operatorname{grad}T) -$$
$$- \operatorname{div}\sum_\alpha \vec{j}_\alpha h_\alpha + \sum_\alpha \rho_\alpha\vec{F}_\alpha\cdot\overline{\vec{V}}_\alpha. \qquad (1.3.38)$$

Using (1.3.24) we obtain

$$\rho\frac{dh}{dt} = \frac{dp}{dt} + \sum_{i=1}^{3}\vec{\tau}_{x_i}\cdot\frac{\partial\vec{v}_0}{\partial x_i} + \operatorname{div}(\varkappa\operatorname{grad}T) - \operatorname{div}\sum_\alpha \vec{j}_\alpha h_\alpha + \sum_\alpha \rho_\alpha\vec{F}_\alpha\cdot\overline{\vec{V}}_\alpha. \qquad (1.3.39)$$

It is not difficult to establish the identity between hydrodynamic equations obtained from the kinetic theory of gases and equations derived phenomenologically. It can be shown that equations obtained by phenomenological means are free from certain limitations (as, for example, taking into account only two-body collisions) which are superimposed on the Boltzmann equation. How-

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ever, in fact, transfer coefficients of the gas mixture are ob-
tained by solving the Boltzmann equation. During chemical reactions
triple collisions are important. Below we shall assume that the
equations written out are correct when reactions occur via triple
collisions in the gas mixture (see section 4, subsection 2).

Thus, equations (1.3.27), (1.3.29), (1.3.31), (1.3.32) and
(1.3.39) form a system of aerothermochemical equations which de-
scribe the chemically nonequilibrium nonstationary flow of the gas
mixture. Let us write them out together again [8].

$$\frac{\partial}{\partial t}\rho c_\alpha + \mathrm{div}(\rho c_\alpha \vec{v}_0 + \vec{j}_\alpha) = R_\alpha;$$

$$\rho \frac{\partial \vec{v}_0}{\partial t} + \rho \vec{v}_0 \,\mathrm{div}\, \vec{v}_0 = \sum_\alpha \rho_\alpha \vec{F}_\alpha - \mathrm{grad}\, p + \sum_{i=1}^{3} \frac{\partial \vec{\tau}_{x_i}}{\partial x_i};$$

$$\rho \frac{\partial}{\partial t} \sum_\alpha c_\alpha h_\alpha + \rho \vec{v}_0 \cdot \mathrm{grad} \sum_\alpha c_\alpha h_\alpha = \frac{\partial p}{\partial t} + \vec{v}_0 \cdot \mathrm{grad}\, p + \sum_{i=1}^{3} \vec{\tau}_{x_i} : \frac{\partial \vec{v}_0}{\partial x_i} +$$

$$+ \mathrm{div}(\varkappa\, \mathrm{grad}\, T) - \mathrm{div} \sum_\alpha \vec{j}_\alpha h_\alpha + \sum_\alpha \rho_\alpha \vec{F}_\alpha \cdot \vec{V}_\alpha, \quad \alpha = 1, \dots, \mu.$$

(1.3.40)

Let us supplement these equations with equations resulting from
equations of continuity for the components:
   gas mixture equations of continuity

$$\frac{\partial \rho}{\partial t} + \mathrm{div}\, \rho \vec{v}_0 = 0;$$

(1.3.41)

equation of continuity for the element

$$\frac{\partial}{\partial t} \rho \sum_\alpha \frac{n_{\tau\alpha} c_\alpha}{M_\alpha} + \mathrm{div} \sum_\alpha \frac{n_{\tau\alpha}}{M_\alpha}(\rho c_\alpha \vec{v}_0 + \vec{j}_\alpha) = 0, \quad \tau = 1, \dots, \nu.$$

(1.3.42)

4. Enskog Method for Solving the Boltzmann Equation

1. Enskog Method for a Nonreacting Gas Mixture

First let us present a scheme for solving the Boltzmann equa-
tion for a gas mixture in which there are no chemical reactions.
For a gas in a homogeneous stationary state with no external forces
the Boltzmann equation is written in the form

$$\sum_{j=1}^{\mu} \iiint (f'_\alpha f'_j - f_\alpha f_j) g_{\alpha j}\, b\, db\, d\varepsilon\, d\vec{v}_j = 0.$$

(1.4.1)

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[8]Where it will not lead to misunderstanding the subscript "0" for
the mean mass velocity $\vec{v}_0$ will be omitted.

Applying the Thomson microscopic reversibility principle, according to which in a state of equilibrium the effect of a collision of each type is balanced by the effect of an inverse collision, we conclude that each term of the sum (1.4.1) must be converted to zero:

$$\iiint (f'_\alpha f'_j - f_\alpha f_j) g_{\alpha j} b\, db\, d\varepsilon\, d\vec{v}_j = 0. \qquad (1.4.2)$$

The condition

$$f'_\alpha f'_j = f_\alpha f_j \qquad (1.4.3)$$

is necessary (see[1.4])and sufficient for converting the integral (1.4.3) into zero. From (1.4.3) it follows that $\ln f$ is an additive invariant of the collisions and if the thermal energy of the molecules includes only chaotic movement energy we will obtain

$$\ln f = \alpha^{(1)} + \vec{\alpha}^{(2)} m\vec{v} + \alpha^{(3)} m\vec{v}^{\,2}/2. \qquad (1.4.4)$$

The normal form of the Maxwell distribution function follows [4] from (1.4.4) :

$$f_\alpha = n_\alpha \left(\frac{m_\alpha}{2\pi k T}\right)^{3/2} e^{-\frac{m_\alpha \vec{v}_\alpha^2}{2kT}}. \qquad (1.4.5)$$

Now let the collisions be so frequent that the velocity distribution is similat ti the lical Maxwell distribution. Then, following Enskog, let us present the function f_α in the form of the following series:

$$f_\alpha = \frac{1}{\delta} f_\alpha^{(0)} + f^{(1)} + \delta f^{(2)} + \cdots, \qquad (1.4.6)$$

where $1/\delta$ is a measure of the sollision frequency. Substituting series (1.4.6) into the Boltzmann equation

$$\frac{\partial f_\alpha}{\partial t} + \vec{v}_\alpha \cdot \frac{\partial f_\alpha}{\partial \vec{r}} + \vec{F}_\alpha \cdot \frac{\partial f_\alpha}{\partial \vec{v}_\alpha} = \sum_{j=1}^{\mu} \iiint (f'_\alpha f'_j - f_\alpha f_j) g_{\alpha j} b\, db\, d\varepsilon\, d\vec{v}_j \qquad (1.4.7)$$

and equating the coefficients with identical powers of δ, we obtain

$$0 = \sum_j J(f_\alpha^{(0)}, f_j^{(0)}); \qquad (1.4.8)$$

$$D^{(0)} \equiv \frac{\partial f_\alpha^{(0)}}{\partial t} + \vec{v}_\alpha \cdot \frac{\partial f_\alpha^{(0)}}{\partial \vec{r}} + \vec{F}_\alpha \cdot \frac{\partial f_\alpha^{(0)}}{\partial \vec{v}_\alpha} = \sum_j [J(f_\alpha^{(0)}, f_j^{(1)}) + J(f_j^{(0)}, f_\alpha^{(1)})]; \qquad (1.4.9)$$

$$D^{(1)} \equiv \frac{\partial f_\alpha^{(1)}}{\partial t} + \vec{v}_\alpha \cdot \frac{\partial f_\alpha^{(1)}}{\partial \vec{r}} + \vec{F}_\alpha \cdot \frac{\partial f_\alpha^{(1)}}{\partial \vec{v}_\alpha} = \sum_j [J(f_\alpha^{(0)}, f_j^{(2)}) + J(f_\alpha^{(1)}, f_j^{(1)}) + J(f_\alpha^{(2)}, f_j^{(0)})]. \qquad (1.4.10)$$

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$$J = \iiint (f_\alpha'^{(l)} f_j'^{(r)} - f_\alpha^{(l)} f_j^{(r)}) g_{\alpha j} \, b \, db \, d\epsilon \, d\vec{v}_j. \tag{1.4.11}$$

Equations (1.4.8) - (1.4.10) are obtained by equating the coefficients respectively with $1/\delta^2$, $1/\delta$ and δ^0. Equations of the type (1.4.8) - (1.4.10) are much simpler than the initial Boltzmann equation since they are linear integral equations. Let us note that the left-hand side of the equations ($D^{(k)}$ operators) is known from the preceding approximation. Solving the equation of the first approximation (1.4.8) is the same as solving a Maxwell distribution. If we require that the conditions be fulfilled:

$$\int f_\alpha^{(0)} d\vec{v}_\alpha = n_\alpha; \tag{1.4.12}$$

$$\sum_\alpha m_\alpha \int \vec{v}_\alpha f_\alpha^{(0)} d\vec{v}_\alpha = \rho \vec{v}_0; \tag{1.4.13}$$

$$\sum_\alpha \int \frac{m_\alpha \vec{V}_\alpha^2}{2} f_\alpha d\vec{v}_\alpha = \frac{3}{2} \sum_\alpha n_\alpha k T, \tag{1.4.14}$$

then the first approximation coincides with the distribution function which corresponds to the local Maxwell distribution. Obviously then the distribution functions of the following approximations must satisfy the conditions:

$$\int f_\alpha^{(k)} d\vec{v}_\alpha = 0; \tag{1.4.15}$$

$$\sum_\alpha m_\alpha \int \vec{v}_\alpha f_\alpha^{(k)} d\vec{v}_\alpha = 0; \tag{1.4.16}$$

$$\sum_\alpha m_\alpha \int \vec{V}_\alpha^2 f_\alpha^{(k)} d\vec{v}_\alpha = 0, \quad k = 1, 2, \dots. \tag{1.4.17}$$

In books by Chapman and Cowling [1] and Hirshfelder it was shown that the conditions in (1.4.15) - (1.4.17) are sufficient for the single-valued determination of the functions $f_\alpha^{(k)}$ ($k \geq 1$). Chapman and Cowling solved integral equations by expanding the unknown integrands into a Sonin polynomial series which are suitable as a result of their orthogonality conditions [1]. The solution to the obtained system of linear algebraic equations of an infinite series on the basis of the Cramer rule is in the form of a ratio of determinants of the infinite series. The determinants converge rapidly with an increase in the number of approximation, and usually the second approximation is sufficient for determining the transfer coefficients (in addition to the thermodiffusion coefficient). These calculations are very tedious. Their detailed presentation   /32 is contained in the above-mentioned works [1,4]. Therefore we will give below (Chapter 1, Section 5) only the specific formulas for calculating transfer coefficients.

2. Enskog Method for a Reacting Gas Mixture

Up until now the Boltzmann equation for a case when chemical reactions occur in a gas has not been solve. However, Prigogine [8,9] studied the perturbation of the Maxwell distribution function in a homogenous gas as a result of the occurrence of chemical reactions of a special type. Let us give some definitions. As we have already mentioned all the elementary processes of gas reaction in a gas can be divided into 3 groups (using terminology from works by Prigogine [8,9]: (1) elastic processes; (2) superelastic processes and (3) inelastic processes. Let us distinguish these groups in the following way:

(1) Those processes as a result of which the sum of the kinetic energies of the particles does not change are called elastic processes.

(2) Inelastic processes are those which result in a decrease of the kinetic energies of the centers of gravity of the particles after a reaction.

(3) Superelastic processes are those which result in an increase of the sum of the kinetic energies of the centers of gravity of the partners after the reaction.

As an example let us examine an excitation reaction of the type

$$A_0 + B \rightleftharpoons A_1 + B. \qquad (1.4.I)$$

The discussion given below is easily transferred to reactions of the type

$$A + B \rightleftharpoons C + D. \qquad (1.4.I')$$

Let us write the law of conservation of mass

$$m_{A_0} = m_{A_1}, \qquad (1.4.18)$$

of momentum

$$m_A \vec{v}_{A_0} + m_B \vec{v}_B = m_A \vec{v}_{A_1} + m_B \vec{v}'_B = (m_A + m_B)\vec{G}, \qquad (1.4.19)$$

of energy

$$u_{A_0} + \frac{1}{2} m_A \vec{v}_{A_0}^2 + \frac{1}{2} m_B \vec{v}_B^2 = u_{A_1} + \frac{1}{2} m_A \vec{v}_{A_1}^2 + \frac{1}{2} m_B \vec{v}'^2_B, \qquad (1.4.20)$$

where u_{A_0} and u_{A_1} are electron energies of the molecules A_0 and A_1.

Let us introduce the relative velocities of the colliding particles:

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$$\vec{v}_{A_1} - \vec{v}'_B = \vec{g}';$$

$$\vec{v}_{A_0} - \vec{v}_B = g.$$

(1.4.22)

Then from (1.4.19), (1.4.21) and (1.4.22) it follows:

$$\vec{v}_{A_0} = \vec{G} + \frac{m_B}{m_A + m_B}\vec{g}; \qquad \vec{v}_B = \vec{G} - \frac{m_A}{m_A + m_B}\vec{g};$$

(1.4.23)

$$\vec{v}_{A_1} = \vec{G} + \frac{m_B}{m_A + m_B}\vec{g}'; \qquad \vec{v}'_B = \vec{G} - \frac{m_A}{m_A + m_B}\vec{g}'.$$

(1.4.24)

Equations (1.4.23) and (1.4.24) give us a concept of particle veloci-
ties via the velocity of the center of the masses and relative to
the velocity of the colliding particles. Using (1.4.23) and (1.4.24)
let us reduce the equation of energy (1.4.20) to the form

$$\frac{1}{2}\frac{m_A m_B}{m_A + m_B}(g^2 - g'^2) = u_{A_1} - u_{A_0}.$$

(1.4.25)

Thus, the difference in the relative kinetic energies of the colli-
ding particles equals the difference in the potential energies. If
we assume that there is no molecular rotation or vibration or if
we disregard their effect then u_α and u_{A_0} represent the formation
enthalpies at 0°K, and consequently the heat Q of the reaction
(1.4.1) is determined from the equation

$$h^0_{A_1} - h^0_{A_0} = -Q_I.$$

(1.4.26)

If we symbolize the relative kinetic energy of the molecules prior
to and after collision by η and η' respectively and the difference
in potential energies by η_{12}, the equation of energy (1.4.25) is
rewritten in the form

$$\eta - \eta' = \eta_{12} = -Q_I.$$

(1.4.27)

Let $\eta_{12} > 0$ (the reaction is endothermic). Then inelastic collisions
occur, if

$$\eta = \frac{1}{2}\frac{m_A m_B}{m_A + m_B}g^2 \geq \eta_{12}.$$

(1.4.28)

The inequality (1.4.28) is the limitation superimposed on the
initial relative molecular velocity. Superelastic collisions
($\eta_{12} < 0$, exothermic reactions) occurs at all positive values of η.

Let us symbolize the probability of an inelastic collision by

$\sigma*(g)$ and the probability of a superelastic collision by $\sigma**(g')$. And let us assume that reaction (1.4.1) going from left to right is endothermic. Let us find the bond which must exist between the functions $\sigma*$ and $\sigma**$ for the principle of microscopic reversibility to be satisfied. The number of A_0 molecules per unit volume (whose velocity is $\vec{v}_{A_0}$, $d\vec{v}_{A_0}$) which leave the region of $d\vec{v}_{A_0}$ velocities per unit of time as a result of inelastic collisions with B molecules and whose velocites are $\vec{v}_B$, $d\vec{v}_B$, will be

$$\int_{A_0} \int_B \sigma^* \, gb\,db\,d\varepsilon\,d\vec{v}_{A_0}\,d\vec{v}_B \,. \tag{1.4.29}$$

The number of A_0 molecules with velocities of $\vec{v}_{A_0}$, $d\vec{v}_{A_0}$ which appear per unit volume per unit of time as a result of superelastic collisions between A_1 molecules (whose velocities are $\vec{v}_{A_1}$, $d\vec{v}_{A_1}$) and B molecules (velocities $\vec{v}'_B, d\vec{v}'_B$) will be

$$\int_{A_1} \int_B' \sigma^{**} \, g'b'\,db'\,d\varepsilon\,d\vec{v}_{A_1}\,d\vec{v}'_B . \tag{1.4.30}$$

The following relationship exists between the relative velocity of g-molecules prior to an inelastic collision and their relative kinetic energy:

$$g = \alpha\eta^{1/2} \,, \tag{1.4.31}$$

where

$$\alpha = 2(m_A + m_B)/m_A m_B . \tag{1.4.32}$$

A similar relationship exists between g' and η'. Let us convert $d\vec{v}_{A_0} d\vec{v}_B$ and $d\vec{v}_{A_1} d\vec{v}'_B$ using (1.4.23) and (.4.24):

$$d\vec{v}_{A_0}\,d\vec{v}_B = d\vec{G}d\vec{g} = g^2 d\Omega\,dg\,d\vec{G} = \tfrac{1}{2}\alpha^3\,\eta^{1/2}\,d\eta\,d\Omega\,d\vec{G}; \tag{1.4.33}$$

$$d\vec{v}_{A_1}\,d\vec{v}'_B = d\vec{G}'\,d\vec{g}' = g'^2 d\Omega\,dg'\,d\vec{G}' = \tfrac{1}{2}\alpha^3\,\eta'^{1/2}\,d\eta'\,d\Omega\,d\vec{G}', \tag{1.4.34}$$

where $d\Omega$ is an element of the solid angle.

From laws of the conservation of momentum (1.4.19) and the conservation of energy (1.4.27) it follows accordingly

$$d\vec{G} = d\vec{G}'; \tag{1.4.35}$$
$$d\eta = d\eta'. \tag{1.4.36}$$

Finally similar geometric collision parameters can be chosen. Then as a result of (1.4.33) - (1.4.36) [cf.(1.1.28)]

$$\eta^{-\frac{1}{2}}d\vec{v}_{A_o}d\vec{v}_B = \eta'^{-\frac{1}{2}}d\vec{v}_{A_1}, d\vec{v}'_B.$$

Applying (1.4.29) and (1.4.30) let us find the information velocity $K_{A_0}d\vec{v}_{A_0}$ of the A_0 molecules (whose velocity is in the range $\vec{v}_{A_0}, d\vec{v}_{A_0}$ as a result of the chemical reaction (1.4.1):

$$K_{A_o} = \iiint \left(f_{A_1} f'_B \sigma^{**} \frac{\eta'}{\eta} - f_{A_o} f_B \sigma^* \right) g_{A_oB} bdbd\varepsilon d\vec{v}_B. \qquad (1.4.38)$$

With equilibrium due to the principle of microscopic reversibility this expression must be identically equal to zero. If we substitute the Maxwell distribution functions, then from (1.4.38) it follows

$$\sigma^* = \sigma^{**} \frac{n_{A_1}}{n_{A_o}} \frac{\eta'}{\eta} e^{\frac{\eta-\eta'}{kT}}. \qquad (1.4.39)$$

This is the desired relationship between the functions σ^* and σ^{**}.

The equation for determining the reaction rate:

$$R_{A_o} = m_{A_o} \iiiint (f_{A_1} f'_B \sigma^{**} \frac{\eta'}{\eta} - f_{A_o} f_B \sigma^*) g_{A_oB} bdbd\varepsilon d\vec{v}_B d\vec{v}_{A_o}. \qquad (1.4.40)$$

Now it is easy to write the integral-differential Boltzmann equation for the case being studied:

$$\frac{\partial f_{A_o}}{\partial t} + \vec{v}_{A_o} \cdot \frac{\partial f_{A_o}}{\partial \vec{r}} + \vec{F}_{A_o} \cdot \frac{\partial f_{A_o}}{\partial \vec{v}_{A_o}} = \left(\frac{\partial_e f_{A_o}}{\partial t} \right)_{A_o} + \left(\frac{\partial_e f_{A_o}}{\partial t} \right)_{A_1} + \left(\frac{\partial_e f_{A_o}}{\partial t} \right)_B + \left(\frac{\partial f_{A_o}}{\partial t} \right)_r, \qquad (1.4.41)$$

where the first three terms represent elastic collisions with A_0, A_1 and B molecules, respectively.

$$(\partial_e f_{A_o}/\partial t)_{A_o} = \iiint (f'_{A_o} f' - f_{A_o} f) \sigma g_{A_o} bdbd\varepsilon d\vec{v}_{A_o} = J(f f_{A_o}); \qquad (1.4.42)$$

$$(\partial_e f_{A_o}/\partial t)_{A_1} = \iiint (f'_{A_o} f'_{A_1} - f_{A_o} f_{A_1}) \sigma g_{A_o A_1} bdbd\varepsilon d\vec{v}_{A_1} = J(f_{A_o} f_{A_1}); \qquad (1.4.43)$$

$$(\partial_e f_{A_o}/\partial t)_B = \iiint (f'_{A_o} f'_B - f_{A_o} f_B) \sigma g_{A_oB} bdbd\varepsilon d\vec{v}_B = J(f_{A_o} f_B); \qquad (1.4.44)$$

$$(\partial f_{A_o}/\partial t)_r = \iiint (f_{A_1} f'_B \sigma^{**} \frac{\eta'}{\eta} - f_{A_o} f_B \sigma^*) g_{A_oB} bdbd\varepsilon d\vec{v}_B = C_{A_o}(f_{A_o} f_B). \qquad (1.4.45)$$

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Let us assume that σ* depends on the relative kinetic energy
of the molecules. Let

$$\sigma^* = 1 - e^{-ag^2},$$ (1.4.46)

where a is the parameter depending on the activation energy. By
activation energy we mean that minimum energy which colliding par-
ticles must possess in order to enter a chemical reaction. We will
say more about this in detail in the second chapter, but now let
us say only that condition (1.4.46) is not the only one of the pos-
sible conditions. In fact, we may assume that:

$$\left. \begin{array}{l} \sigma^* = 0 \text{ with } g < g_0 ; \\ \sigma^* = 1 \text{ with } g \ge g_0 . \end{array} \right\}$$ (1.4.47)

Condition (1.4.46), as we can easily see, gives for σ* a value
equal to 0 at $g \to 0$ and $\sigma \to 1$ at $g \to \infty$.

Reaction coordinate
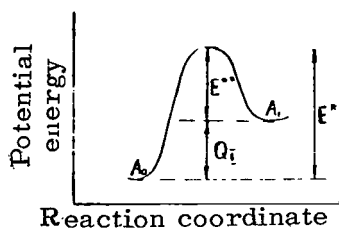
Fig. 3.

In Fig. 3 the dependence of the potential
molecular energy on the reaction coordinate
is represented. Also the activation energy E^*
of a direct endothermic reaction and of an in-
verse exothermic reaction is indicated (with-
out taking into account quantum effects). As
we can easily see from Figure 3

$$E^* = E^{**} + Q_I .$$ (1.4.48)

In Prigogine's paper [8] an evaluation of the perturbation of the
Maxwell function as a result of the reaction (1.4.1) was obtained
by the Enskog method:

$$f_\gamma^{(1)} \cong -\frac{51}{16} n_\gamma \left(\frac{m_\gamma}{2\pi kT} \right)^{3/2} e^{-\frac{m_\gamma \vec{V}_\gamma^2}{2kT}} \frac{Q_I}{E^*} \left(\frac{15}{4} - 5 \frac{m_\gamma}{2kT} \vec{V}_\gamma^2 + \right.$$

$$\left. + \left(\frac{m_\gamma}{2kT} \right)^2 \vec{V}_\gamma^4 \right) x_{A_0} x_B , \quad \gamma = A_0, A_1, B; \ x_\gamma = n_\gamma / \sum_\gamma n_\gamma .$$ (1.4.49)

Finally, let us find the reaction rate (1.4.1) in the simple
case when a reaction is just beginning and the concentration of
the A_1 molecules can be disregarded. In this case the reaction
rate [see (1.4.40)]

$$R_{A_0} = -m_{A_0} \iiiint f_{A_0} f_B \sigma^* g_{A_0 B} b \, db \, d\varepsilon \, d\vec{v}_B \, d\vec{v}_{A_0} .$$ (1.4.50)

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If we symbolize the value of the reaction rate which corresponds to the Maxwell distribution by $R_{A_0}^{(0)}$, then

$$R_{A_0} \cong R_{A_0}^{(0)} (1 + 1,2 x_{A_0} x_B Q_I / E^*).\qquad(1.4.51)$$

From (1.4.51) we see that for an exothermic reaction ($Q_1 > 0$ is an inverse reaction in our case) the perturbation of the balanced distribution increases the reaction rate. This increase is greater the larger the ratio of the heat of reaction to the activation energy. Conversely, for an endothermic reaction (the direct reaction in our case) the rate will decrease. But the heat Q_1 of the endothermic reaction can not become larger, with respect to absolute value, than the activation energy E^*. Therefore, the maximum decrease is $\sim [1 - 1.2\ x_A\ x_B]$ and does not exceed 25%. On the contrary, for an exothermic reaction there is no upper limit of this effect.

Let us study another example. Let a chemical reaction take place in a gas which was initially in a stationary uniform state

$$A + A \longrightarrow B + C. \qquad (1.4.II)$$

Let us assume that the reaction is just beginning so that we can disregard all the collisions between A and B or A and C. Let σ^* be the probability of an inelastic collision of the A molecules. And we may disregard the heat of reaction (1.4.11). The contribution of elastic collisions to df/dt is determined by the equation

$$\iiint (f'f_1' - ff_1)(1 - \sigma^*) g b\, db\, d\varepsilon\, d\vec{v}_1, \qquad (1.4.52)$$

and of inelastic collisions

$$- \iiint ff_1 \sigma^* g b\, db\, d\varepsilon\, d\vec{v}_1. \qquad (1.4.53)$$

Since the heat of reaction (1.4.11) is assumed to be negligibly small σ^* has the same value for direct and inverse collisions. Thus the Boltzmann equations:

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \frac{\partial f}{\partial \vec{r}} + \vec{F} \cdot \frac{\partial f}{\partial \vec{v}} = \iiint (f'f_1' - ff_1) g b\, db\, d\varepsilon\, d\vec{v}_1 -$$
$$- \iiint f_1' f' \sigma^* g b\, db\, d\varepsilon\, d\vec{v}_1. \qquad (1.4.54)$$

For the case (1.4.46) an estimation of the perturbation function $f^{(1)}$ has the form [9]

$$f^{(1)} = -n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mV^2}{2kT}} \frac{45}{126} \frac{kT}{E^*} \left(1 - \frac{4}{3}\vec{V}^2 + \frac{4}{15}\vec{V}^4\right). \tag{1.4.55}$$

The reaction rate

$$R = -m_A \iiiint f'f_1' \sigma^* g\, db\, d\varepsilon\, d\vec{v}_1\, d\vec{v}. \tag{1.4.56}$$

For the case in (1.4.46)

$$R = R^{(0)}\left(1 - \frac{9}{256}\frac{kT}{E^*}\right), \tag{1.4.57}$$

where $R^{(0)}$ is the reaction rate in the assumption of the Maxwell distribution. From (1.4.55) it is evident that the change in reaction speed and the perturbation function $f^{(1)}$ are small for the normal values of E^*/kT. Even for $E^*/kt \sim 5$ the error committed as a result of using $R^{(0)}$ instead of R is on the order of 1%.

For the case of (1.4.47)

$$R = R^{(0)}\left\{1 - \frac{1}{32}e^{-E^*/kT}\left(\frac{E^*}{kT}\right)^3\left[\left(\frac{E^*}{kT}\right)^2 - 5\frac{E^*}{kT} + \frac{17}{2}\right]\right\}. \tag{1.4.58}$$

Let us compare this formula with (1.4.57). The reaction rates depend substantially on the choice of the function σ^*. For $E^*/kt = 5$ (1.4.58) yields

$$R = 0.77R^{(0)}$$

This decrease in R now is $\sim$ 20% in comparison with 1% from (1.4.57). The precise value of R depends on the analytical form of σ^* which must be obtained from quantum chemistry. As yet no such calculations for reactions of practical interest have been made.

Thus, at least for the 1st and 2nd types of reactions which we have studied perturbation of the distribution function is not great, if

$$kT/E^* \ll 1, \quad |\zeta/E^*| \ll 1. \tag{1.4.59}$$

Let us assume that the conditions of (1.4.59) determine the perturbation of the distribution function for all types of reactions. Therefore, if the conditions of (1.4.59) are carried out, in the calculations we can use the transfer coefficients for the nonreact-

ing gas mixture. As an example let us examine the dissociation reaction

$$O_2 \rightleftharpoons 2O;$$ (1.4.III)
$$N_2 \rightleftharpoons 2N;$$ (1.4.IV)
$$NO \rightleftharpoons N + O.$$ (1.4.V)

The first of the conditions of (1.4.59) can be rewritten in the form

$$E^*/k >> T$$

Then

Reaction	E^*. kCal/mole	E^*/k,°K
(1.4.III)	118	59,400
(1.4.IV)	225	113,000
(1.4.V)	150	75,000

Thus, the characteristic temperatures for E^*/k are usually substantially higher than the maximum temperatures studied in aerothermochemistry (~ 10,000° - 12,000°K). The second of the conditions of (1.4.59) is not carried out as well, since generally the heats of chemical reactions are comparable, with respect to order of magnitude, with the activation energy. Nevertheless, everywhere below the transferable properties of the gas will be calculated on the basis of formulas for a nonreacting gas mixture.

3. Influence of Internal Degrees of Freedom on the Transfer Phenomenon.

So far we have assumed that internal and translational degrees of freedom are energetically balanced. However, if in a gas the balanced energy distribution with respect to degrees of freedom is destroyed (a typical case is the passage of the gas through a strong shock wave) then different degrees of molecular freedom take a different time to come into equilibrium (which is called the relaxation time) or likewise they come into equilibrium at a different characteristic distance (which is called the relation distance). This is due to the fact that in order to establish equilibrium in the translational degrees of freedom only some collisions are required (hence follows in particular the fact that the width of the shock wave is of the order of the length of the free molecular path) and the rotational degrees of freedom are balanced every 10-50 collisions. Finally, the Maxwell distribution in the energy spectrum of vibrational degrees of freedom is established for a greater number of collisions (up to 5000). Thus, the rate of rotational energy transfer during molecular collisions is comparable to the rate of translational energy transfer. However, for vibrational degrees of freedom to be energetically balanced with the transitional degrees, $10^4 - 5 \cdot 10^4$ collisions are required. If L is

the characteristic length of the streamlined material, l_t and l_i are the relaxation lengths of the translational and internal degrees of freedom, respectively, and l_{ti} is the length of equilibrium established between the translation and internal degrees of freedom, then we can separate out the following cases of streamline flow:

(1) $l_t \sim l_i \sim l_{ti} \gg L$ represent the "frozen" flows: /40

(2) $l_t \sim l_i \sim l_{ti} \ll L$ represent the "quasi-equilibrium" single temperature flows. In this case the relaxation phenomena occur via the mechanism of volumetric (or as it is called-second) viscosity;

(3) $l_t \ll l_i \sim l_{ti} \sim L$ is the so-called relaxation of the mixture [10].

(4) $l_t \sim l_i \ll l_{ti} \sim L$ represents the two-temperature relaxation. This case corresponds, for example, to the physically realistic process when the equilibrium between the translational and vibrational degrees of freedom is established much more slowly than within the respective degrees of freedom. The two-temperature relaxation was studied in detail in papers by V.N. Zhigulev [11] and V.M. Kuznetsov [12].

We can easily take into account the contribution of the internal degrees of molecular freedom to heat transfer if the rate of energy transfer from the internal to the translational degrees of molecular freedom is so great that the balanced distribution of energy is established with respect to the degrees of molecular freedom and corresponds to the local temperature.

Let there be a gas whose molecules can be found in various quantum states of N_j. We will look at all the quantum states of molecules as separate chemical materials. The density of the energy flux in second approximation is determined by the formula

$$\vec{q} = -\varkappa^{(0)} \frac{\partial T}{\partial \vec{r}} + \sum_j n_j h_j \vec{V}_j ,$$

(1.4.60)

where $\varkappa^{(0)}$ is the coefficient of thermal conductivity of the gas when the molecules do not have internal degrees of freedom. In writing (1.4.60) we have taken into account the fact that in a good approximation the internal molecular energy (not as a result of the translational motion) does not depend on velocity. But $h_j = \frac{5}{2}kT + E_j^{(int)}$ [see (1.2.35)]. If we allow for the fact that for electron-unexcited molecules the coefficients of diffusion are the same irrespective of the quantum state, then

$$\vec{V}_j = -\frac{n}{n_j} D \frac{\partial}{\partial \vec{r}} \left(\frac{n_j}{n} \right) ,$$

(1.4.61)

where D is the coefficient of self-diffusion (see section 5 of this chapter).

Let us use $x_j = n_j/n$. Then using (1.4.61) we can rewrite (1.4.60) in the form

$$\vec{q} = -(x^{(0)} + nD\sum_j h_j \, \partial x_j / \partial T) \, \partial T / \partial \vec{r}. \tag{1.4.62}$$

Thus

$$x = x^{(0)} + nD\sum_j h_j \, \partial x_j / \partial T. \tag{1.4.63}$$

The enthalpy of the gas mixture is determined by the equation

$$H = \sum_j x_j \, h_j \,,$$

and the heat capacity at a constant pressure,

$$c_p = \frac{d}{dT} \sum_j x_j h_j = \sum_j x_j \frac{dh_j}{dT} + \sum_j h_j \frac{\partial x_j}{\partial T}. \tag{1.4.64}$$

The first term in (1.4.64) is the specific heat of the gas if the molecules do not have internal degrees of freedom, i.e., $\frac{5}{2} k$. Thus,

$$x = x^{(0)} + nD(c_p - 5k/2). \tag{1.4.65}$$

Let us introduce the dimensionless parameter

$$\delta_f = \frac{5k}{2} \frac{nD}{x^{(0)}}, \tag{1.4.66}$$

then

$$x/x^{(0)} = (1 - \delta_f) + \frac{2}{5k} c_p \, \delta_f. \tag{1.4.67}$$

The right-hand term of (1.4.67) is the so-called Eucken correction for the internal degrees of molecular freedom. Hirshfelder [13] found that for the Lennard-Jones potential and the Buckingham potential $\delta f = 0.885$ within 2% (Eucken himself found a value of 2/3 for δ_f from very simplified representations). Thus

$$x = x^{(0)} (0.115 + 0.354 c_p / k). \tag{1.4.68}$$

5. Molecular Transfer Coefficients

The molecular transfer coefficients given below were obtained by solving the Boltzmann equation during whose derivation it was assumed that the molecular diameter is small in comparison with the mean distance between the molecules and triple collisions were not studied. These assumptions are correct only for rarefied gases. Also, generally, rather precise expressions for the coefficients are obtained in assuming that the gas is monatomic. However, as

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we already mentioned the internal degrees of freedom exert a very
small influence on the coefficients of diffusion and shear viscosity
although in calculating the coefficient of thermal conductivity we
must take into account the internal degrees of molecular freedom.
During the flow of a chemically reacting gas, triple molecular
collisions can be very substantial (as we know, recombination re-
actions go through triple collisions). Therefore, the formulas
used below for the transfer coefficients and for the gas flows in
which reactions going through triple collisions occur are considered
formally correct. This assumption is justified by the fact that
molecular collisions which lead to chemical reactions are relatively
rare and do not lead to a substantial distortion of the distribution
function (see Section 4, subsection 2). Thus, the results obtained
have a wider range of applicability than follows from theory. Let
us also note that the strict kinetic theory of dense gases and
fluids has been significantly less developed than the theory of
rarefied gases. Therefore, we must use molecular transfer coeffi-
cients for rarefied gases. However, it has been empirically es-
tablished that, for example, the formula relating diffusion currents
to concentration gradients of multicomponent mixtures (given in
the theory of rarefied gases) is quite appropriate for dense gases
and fluids [see (1.5.6), subsection 1].

1. Diffusion Coefficients

The diffusion coefficients of a multicomponent mixture can be
obtained in good approximation by taking into account only one term
in a Sonin polynomial expansion:

$$\vec{j}_\alpha = \frac{n^2}{\rho} \sum_{\beta=1}^{\mu} m_\alpha m_\beta \Delta_{\alpha\beta} \vec{d}_\beta ; \qquad (1.5.1)$$

$$d_\beta = \frac{\partial}{\partial \vec{r}}\left(\frac{n_\beta}{n}\right) + \left(\frac{n_\beta}{n} - \frac{n_\beta m_\beta}{\rho}\right)\frac{\partial \ln p}{\partial \vec{r}} . \qquad (1.5.2)$$

In (1.5.1) and (1.5.2) thermodiffusion whose influence is con-
sidered below as unimportant and the effect of external forces is
disregarded

$$[\Delta_{\alpha\beta}]_1 = \frac{F^{\beta\alpha} - F^{\alpha\alpha}}{m_\beta |F|} , \qquad (1.5.3)$$

where $|F|$ is the determinant from $F_{\alpha\beta}$, and $F^{\beta\alpha}$ is its minor:

$$F_{\alpha\beta} = \frac{n_\alpha}{\rho D_{\alpha\beta}} + \sum_{\substack{l=1 \\ l \neq \alpha}}^{\mu} \frac{m_\beta n_l}{\rho m_\alpha D_{\alpha l}} ; \qquad (1.5.4)$$

$$F_{\alpha\alpha} = 0. \qquad (1.5.5)$$

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Below, in presenting numerical calculations in the scope of boundary layer theory, we need a dimensionless form of these equations in Dorodnitsyn variables [see (3.2.6)]:

$$\bar{I}_{\alpha\lambda} = \frac{1}{Pr} \sum_{\beta=1}^{\mu} M_\beta \Lambda_{\alpha\beta} \left[\bar{c}_{\beta\lambda} \sum_{\alpha=1}^{\mu} \bar{c}_\alpha - \bar{c}_\beta \sum_{\alpha=1}^{\mu} \bar{c}_{\alpha\lambda} \right]; \qquad (1.5.6)$$

$$\Lambda_{\alpha\beta} = \frac{Z^{\beta\alpha} - Z^{\alpha\alpha}}{M_\beta |Z|}, \qquad (1.5.7)$$

where the $|Z|$ is the determinant

$$\begin{vmatrix} 0, & z_{12}, & \ldots, & z_{1\mu} \\ z_{21}, & 0, & \ldots, & z_{2\mu} \\ \cdot & \cdot \cdot \cdot \cdot \cdot \cdot \cdot & \cdot \\ z_{\mu 1}, & z_{\mu 2}, & \ldots, & 0 \end{vmatrix}.$$

Elements of this determinant are determined by the formulas

$$z_{\alpha\beta} = \frac{\bar{c}_\alpha}{L_{\alpha\beta}} + \frac{M_\beta}{M_\alpha} \sum_{\substack{k=1 \\ k \neq \alpha}}^{\mu} \frac{\bar{c}_k}{L_{\alpha k}}. \qquad (1.5.8)$$

Here and below, a line means that the pertinent value which characterizes the α-component of the gas mixture refers to the molecular weight M_α. Also, we introduce the designation

$$z_{\alpha\beta} = F_{\alpha\beta} \varkappa / N \rho c_p. \qquad (1.5.9)$$

$\Lambda_{\alpha\beta}$ represents the generalized Lewis coefficients and $L_{\alpha\beta}$ is the Lewis number formed with the help of binary diffusion coefficients, i.e.,

$$\Lambda_{\alpha\beta} = \frac{\rho c_p}{\varkappa} \Delta_{\alpha\beta}; \qquad L_{\alpha\beta} = \frac{\rho c_p}{\varkappa} D_{\alpha\beta}.$$

In deriving (1.5.6) barodiffusion, whose influence in the boundary layer is small in comparison with the concentration diffusion, is disregarded. As we can easily see, calculating diffusion currents in final analysis amounts to calculating diffusion currents /44 of a binary mixture.

In first approximation the binary diffusion coefficient $D_{\alpha\beta}$ (in cm^2/sec) for nonpolar gases is independent of the α and β-component concentrations and is determined by the equation

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$$D_{\alpha\beta} = 0.0026280 \sqrt{T^3 (M_\alpha + M_\beta)/2 M_\alpha M_\beta} \Big/ p \sigma_{\alpha\beta}^2 \Omega_{\alpha\beta}^{(1,1)*}(T_{\alpha\beta}^*).$$ (1.5.10)

In (1.5.10) p is the pressure in atm., T is the temperature, in °K, parameter $\sigma_{\alpha\beta}$ is the diameter of collisions for the α and β molecules, in Å and $\Omega_{\alpha\beta}^{(1,1)*}$ is the dimensionless integral whose value depends on the dynamics of two-body collisions and, therefore, on the law of intermolecular forces (more will be said about this in detail below). The highest approximations of $D_{\alpha\beta}$ are very slightly distinguished from the first:

$$[D_{\alpha\beta}]_k = [D_{\alpha\beta}]_1 f_{D_{\alpha\beta}}^{(k)},$$ (1.5.11)

where for the Lennard-Jones potential the function $f_{D_{\alpha\beta}}^{(k)}$ for the majority of binary mixtures has values from 1.00 to 1.03 [4].

Note. As we can easily see, calculating the diffusion current of the α-component involves finding the value of the determinant of the μth order. Sometimes it is more convenient to use the relationship between the currents and the gradiants of the concentrations in the form

$$\frac{\bar{c}_\beta}{\rho} \sum_{\substack{\alpha=1 \\ \alpha \neq \beta}}^{\mu} \frac{\bar{j}_{\alpha n}}{D_{\alpha\beta}} - \frac{\bar{j}_{\beta n}}{\rho} \sum_{\substack{\alpha=1 \\ \alpha \neq \beta}}^{\mu} \frac{\bar{c}_\alpha}{D_{\alpha\beta}} = \frac{\partial \bar{c}_\beta}{\partial n} \sum_{\alpha=1}^{\mu} \bar{c}_\alpha - \bar{c}_\beta \frac{\partial}{\partial n} \sum_{\alpha=1}^{\mu} \bar{c}_\alpha.$$ (1.5.12)

In writing (1.5.12) the thermodiffusion has been disregarded and the approximation of the boundary layer used. Let us note that the accuracy of the equations in (1.5.12) is the same as in (1.5.6).

2. Viscosity Coefficient

In first approximation the viscosity coefficient is expressed in the form of the ratio of the $\mu + 1$ determinants and the μ-th orders. But since the off-diagonal elements of the determinants are small in comparison with the diagonal elements it is possible to use the following formula in good approximation

$$\eta = \sum_{i=1}^{\mu} \bar{c}_i \Bigg/ \left[\frac{\bar{c}_i}{\eta_i} + 2.308 \sum_{\substack{k=1 \\ k \neq i}}^{\mu} \frac{\bar{c}_k}{\eta_{ik}} \frac{\Omega_{ik}^{(1,1)*}}{\Omega_{ik}^{(2,2)*}} \frac{M_k}{M_i + M_k} \right]$$ (1.5.13)

The coefficient 2.308 was obtained by Buddenberg and Wilke (instead of 10/3 obtained in (1.5.13) in the above approximation) on the basis of analyzing experimental data [14]. For pure nonpolar gases the first approximation for the viscosity coefficient gives

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$$\eta_i = 0.000026693\sqrt{M_i T}/\sigma_i^2 \, \Omega_i^{(2,2)*} \; ,$$

where η_i is expressed in g/cm·sec. Here σ_i is the diameter for the collisions of the i-components and i, $\Omega_i^{(2,2)*}$ is the integral of collisions versus the parameter

$$T_i^* = kT/\varepsilon_i \; ,$$

(1.5.14)

The following was obtained for the coefficient η_{ik} in first approximation

$$\eta_{ik} = 0.000026693\sqrt{2M_i M_k T/(M_i+M_k)}/\sigma_{ik}^2 \, \Omega_{ik}^{(2,2)*}(T_{ik}^*).$$

(1.5.15)

3. *Thermal Conductivity Coefficient*

The thermal conductivity coefficient for a gas mixture is calculated even in first approximation from very complex formulas. Mason and Saxena [15] obtained a much simpler formula for calculating the thermal conductivity coefficient of the mixture. Its derivation is similar to the derivation of the Budenberg and Wilke formula for the viscosity coefficient. Moor and Zlotnik [16] note that the correspondence with experimental data is completely satisfactory and almost better than that obtained on the basis of precise theory.

$$\varkappa = \sum_{i=1}^{\mu} \varkappa_i \left/ \left[1 + \sum_{\substack{k=1 \\ k \neq i}}^{\mu} G_{ik} \frac{\bar{c}_k}{\bar{c}_i}\right]\right. ,$$

(1.5.16)

$$G_{ik} = \frac{1.065}{2\sqrt{2}}\left(1 + \frac{M_i}{M_k}\right)^{-\frac{1}{2}}\left[1 + \left(\frac{\varkappa_i^{(0)}}{\varkappa_k^{(0)}}\right)^{\frac{1}{2}}\left(\frac{M_i}{M_k}\right)^{\frac{1}{4}}\right]^2 ,$$

(1.5.17)

Here $\varkappa_i^{(0)}$ is the thermal conductivity of the pure gas with frozen internal degrees of freedom and $\varkappa_i$ is calculated on the basis of a formula taking into account the Eucken correction

$$\varkappa_i = \varkappa_i^{(0)}(0.115 + 0.354 c_{pi}/R).$$

(1.5.18)

Let us present other formulas for calculating the thermal conductivity coefficient of a pure gas:

$$x_i^{(0)} = 0.00019891 \frac{\sqrt{M_i T}}{M_i \sigma_i^2 \Omega_i^{(2,2)*}} = \frac{n_i}{M_i} \frac{15}{4} R. \tag{1.5.19}$$

Let us look at the uniformity of the values in the above formulas (1.5.16) - (1.5.19): κ_i is measured in cal/cm·sec·deg c_{pi} is in cal/mole·deg, $R = 1.98646$ cal/mole·deg, and the uniformity of n_i in g/cm·sec.

4. *Collision Integrals and Potential Energy Parameters*

To determine the transfer coefficients we must know the potential energy parameters of molecules σ_{ij} and ε_{ij}/k which characterize the reaction of i and j-type molecules. For a pure nonpolar gas the potential $\phi(r)$ of molecular reaction as a function of the distance between the centers of the molecules can be determined by the equation:

$$\varphi(r) = 4\varepsilon_i [(\sigma_i/r)^{12} - (\sigma_i/r)^6]. \tag{1.5.20}$$

The function $\phi(r)$ determined by (1.5.20) is called the Lennard-Jones potential. Figure 4 represents the Lennard-Jones potential and also indicates the molecular reaction parameters.
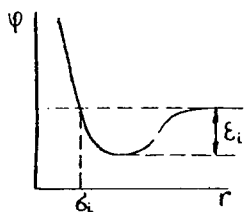

Fig. 4

The σ_{ij} and ε_{ij} force constants must be obtained generally from experiment. However, such measurements of the reaction between two nonidentical molecules do not exist and in practice we must use empirical "combination rules" which relate force constants of identical molecules to the force constants of nonidentical molecules. These rules have the form:

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j); \tag{1.5.21}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}. \tag{1.5.22}$$

Unfortunately, at the present time the force constants of atoms has not been studied very extensively. Hirshfelder and Eliason [17] established empirically that the diameter of an atomic collision is double the mean radius $\overline{r}$ of the electron which is found in the outermost orbit, plus 1.8 Å:

$$\sigma = 2\overline{r} + 1.8 \, \text{Å}. \tag{1.5.23}$$

The value of $\overline{r}$ is calculated on the basis of the Slater screening constants

$$\overline{r} = \frac{1}{2} n^* (2n^* + 1)(Z - S) a_0, \tag{1.5.24}$$

where Z is the atomic number $n*$ is the effective principal quantum number of the outermost shell, S is the Slater screening constant for this shell, a_0 is the radius of the Bohr orbit.

The values of ε_i for atomic components are not known. We were compelled to determine them with numerial calculations of interpolations on the basis of the molecular weights of inert gases. Thus, values for ε_i were obtained for atoms of carbon, nitrogen and oxygen. In Table 3 constants of the reaction forces of certain types of molecules and atoms for the Lennard-Jones potential are given. More complete data can be found in the work by Hirshfelder, et al., [4].

TABLE 3

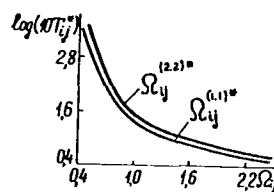| Gas	ε/k,°K	σ, Å
Ne, M = 20,2	27,5	2,858
Ar, M = 39,9	116,0	3,465
Kr, M = 83,8	190,0	3,61
Xe, M = 131,3	229,0	4,055
N_2	79,8	3,749
O_2	88,0	3,541
CO	88,0	3,706
CO_2	213,0	3,897
NO	91,0	3,599
N_2O	237,0	3,816
H	–	3,38
C	–	3,42
N	–	2,88
O	–	2,96
CN	115	3,5
C_3	150	3,6

Fig. 5

The integrals $\Omega_{ij}^{(1.1)*}$ and $\Omega_{ij}^{(2.2)*}$ are included in the expression for the transfer coefficients of pure gases and mixtures (the exception is the thermodiffusion coefficient). The physical sense of these integrals lies in the fact that they point out the distinction between the molecular model used and the solid sphere model. For solid spheres all the values for $\Omega^{(l,s)*} = 1$.

In Figure 5 the collision integrals $\Omega_{ij}^{(1.1)*}$ and $\Omega_{ij}^{(2.2)*}$ are drawn as functions of $\log 10$ T_{ij}^* for the Lennard'Jones model. For other reaction models $\Omega_{ij}^{(1,s)*}$ integrals are tabulated in the Hirshfelder book [4] in the form of a function of $kT/\varepsilon ij$.

CHAPTER 2

ELEMENTS OF CHEMICAL KINETICS

The system of aerothermochemical equations (1.3.40)-(1.3.42) includes the formation rates R_α of the α-component ($\alpha = 1,...,\mu$) as a result of all the reactions in the gas phase. In practice, for the purposes of aerodynamics in calculating the flows with chemical reactions it is enough to know the numerical values of the so-called chemical reaction rate constants. Up until the present time analytical methods of theoretical chemistry have not permitted calculating reaction rate constants, and experiments have been the basic source of information on reaction rates. Therefore below we will give mainly only the most necessary information from phenomenological chemical kinetics.

1. Phenomenological Chemical Kinetics of Homogeneous Gas Chemical Reactions

First let us give some formal symbols and definitions. In chemistry the following definitions of the concentration of components in a gas mixture are often used: c_α is the mass concentration of the component:

$$c_\alpha = \rho_\alpha/\rho = \rho_\alpha/\sum_\alpha \rho_\alpha = m_\alpha n_\alpha / \sum_\alpha m_\alpha n_\alpha,$$

(2.1.1)

w_α is the number of moles of the α-component per unit volume of the mixture:

$$w_\alpha = \rho_\alpha / M_\alpha.$$

(2.1.2)

Therefore,

$$w_\alpha = c_\alpha \rho / M_\alpha = \rho \bar{c}_\alpha.$$

(2.1.3)

The following formula gives the total number of moles of all the components per unit volume

$$w = \sum_\alpha w_\alpha = \rho \sum_\alpha \bar{c}_\alpha.$$

(2.1.4)

By analogy with (2.1.2) let us determine the molecular weight
of the mixture on the basis of the formula

$$M = w/\rho = 1/\underset{\alpha}{\Sigma}\, \bar{c}_\alpha. \tag{2.1.5}$$

x_α is the mole fraction of the α-component (number of moles of the α-component per mole of mixture)

$$x_\alpha = w_\alpha/w = \bar{c}_\alpha/\underset{\alpha}{\Sigma}\,\bar{c}_\alpha. \tag{2.1.6}$$

Below on the whole we will use the concentrations $\bar{c}_\alpha$. Obviously for c_α and x_α the following equations are satisfied:

$$\overset{\mu}{\underset{\alpha=1}{\Sigma}}\, c_\alpha = 1, \quad \overset{\mu}{\underset{\alpha=1}{\Sigma}}\, x_\alpha = 1. \tag{2.1.7}$$

Finally, the equation of state in the c_α concentrations is written as follows:

$$p_\alpha = n_\alpha kT = \rho RT \bar{c}_\alpha; \tag{2.1.8}$$

$$p = \underset{\alpha}{\Sigma}\, p_\alpha = \rho RT \underset{\alpha}{\Sigma}\, \bar{c}_\alpha, \tag{2.1.9}$$

where R is the gas constant ($R = kN = 1.98646$ Cal/mole·deg).

The general stoichiometric equation which describes a reaction occurring at one stage can be represented in the form

$$\overset{\mu}{\underset{\alpha=1}{\Sigma}}\, \nu'_\alpha A_\alpha \longrightarrow \overset{\mu}{\underset{\alpha=1}{\Sigma}}\, \nu''_\alpha A_\alpha. \tag{2.1.10}$$

Thus, if the chemical·component, represented in (2.1.10) by the symbol A_α, is not the original material (the reaction product), then $\nu'_\alpha = 0$ ($\nu''_\alpha = 0$). Let us now list the components (chemical elements and materials) which we will study below in the numerical calculations of gas flows with chemical reactions: $A_1 = C$, $A_2 = CO$, $A_3 = CO_2$, $A_4 = O$, $A_5 = O_2$, $A_6 = N$, $A_7 = N_2$, $A_8 = NO$. For example, let the following reaction take place

$$O_2 \longrightarrow 2O. \tag{2.1.I}$$

Then

$$\nu'_1 = \nu'_2 = \nu'_3 = \nu'_4 = \nu'_6 = \nu'_7 = \nu'_8 = 0, \quad \nu'_5 = 1$$
$$\nu''_1 = \nu''_2 = \nu''_3 = \nu''_5 = \nu''_6 = \nu''_7 = \nu''_8 = 0, \quad \nu''_4 = 2.$$

If we look at the effective chemical reaction which in fact take's place in several stages the coefficients $\nu'_\alpha, \nu''_\alpha$ can not be whole numbers.

The law of mass action is the basic law of phenomenological chemical kinetics. It is physically obvious that only colliding molecules reat. The number of collisions is proportional to the number of molecules per unit volume, and therefore to the concentration of the initial materials:

$$\bar{R}_\alpha = (\nu''_\alpha - \nu'_\alpha) k_f \prod_{j=1}^{\mu} w_j^{\nu'_j}.$$ (2.1.11)

The expression given for the formation rate of the α-component is the basic postulate of chemical kinetics. In (2.1.11) k_f is the chemical reaction rate constant. In general, the rate constant k_f is proportional to the number of collisions of molecules whose energy is equal to or more than the energy E (the activation energy). As a rule, we must also introduce the factor p (the steric factor). The coefficient p takes into account the three-dimensional obstacles to the occurrence of a reaction. Its value in different reactions may fluctuate in the range from 1 to 10^{-8} [19]. If in a gas, there is a molecular distribution with respect to energies that is not very different from the Maxwell distribution, then

$$Z_a = Z e^{-E/RT},$$ (2.1.12)

where Z_α is the number of collisions of molecules whose energy is equal to or more than E, and Z is the total number of collisions per unit time per unit volume. Thus,

$$k_f = p Z_a.$$ (2.1.13)

But the total number of collisions in the gas is proportional to $\sqrt{T}$. Therefore, the general form of expression for the rate constant will be

$$k_f = B T^\beta e^{-E/RT}.$$ (2.1.14)

The temperature dependence of the pre-exponential term is often different from the theoretical value 0.5 for the best correspondence with experimental data. Let us go into more detail about the concept of activation energy. Let there take place a reaction in the gas

$$AB + C \longrightarrow A + BC.$$
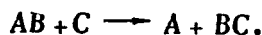
The relative distribution of the AB molecule and the C atom is given in Figure 6. At great distances r_2 the atom C does not react with the molecule AB and the potential energy of the system $AB + C$ /52 is equal to the potential energy of the AB molecule. The curve of the dependence of the potential energy of AB on the distance between the atoms has the form given in Figure 7. The atom A is found at the origin of the coordinates and the nucleus of the other

atom may be found at any distance provided that $r_1 << r_2$. The potential energy curve, as usual, has a deep minimum which represents the equilibrium distance r_{1e} between the atoms in AB. Let us call this minimum the zero potential energy of the system. Having a potential curve on the basis of (2.1.15) we can easily construct a curve of the dependence of force F_1 on the distance between the atoms:
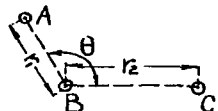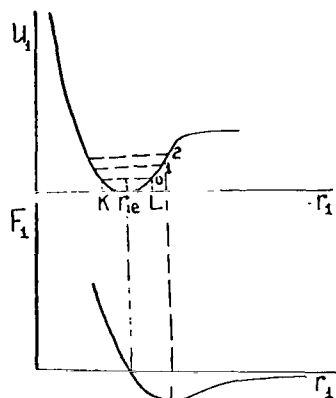
$$F_1 = -du_1/dr_1 .$$

(2.1.15)

Fig. 6

Fig. 7

The shape of the curve $F_1(r_1)$ reflects the known fact that at great distances atoms attract and at small distances they repel. Atoms in a bivalent molecule can vibrate at definite frequencies whose magnitude is determined from quantum mechanics. In Figure 7, the quantum vibrational level for AB is given beginning with the zero vibrational level found at a distance $1/2h\nu$ from the minimum level of potential energy. For the zero level, for example only at distances $r_1 = OK$ and $r_1 = OL$, the entire energy of the system is potential. At other distances it accumulates from the potential and kinetic energy of the system (besides the distance r_{1e} where all the energy is kinetic).

Let the reaction take place and let atom A move away a distance $r_1 >> r_2$. Then the potential energy U_2 of the system accumulates from the potential energy of the molecule BC. In Figure 8 two hypothetical curves of the dependence of the potential energies U_1 and U_2 on the distance between the atoms are drawn. Let the transfer from the zero vibrational level to the zero level occur. From Figure 8 it is evident that to transfer through the potential barrier, atom C must have energy no less than the activation energy E. The change in potential energy of the system of atoms A,B,C along the reaction coordinate r is given in Figure 9. The area δ represents the transition state. From Figure 9 it is evident that the transition from state $AB + C$ to state $BC + A$ is possible only with energy E_1 and the reverse transition is possible only with energy E_2. With the occurrence of a reaction in a forward direction the following amount of energy is extracted.

$$Q = E_2 - E_1 .$$

(2.1.16)

In this case $Q < 0$, the energy is absorbed and, therefore, the forward reaction is endothermic. Let us note that if there is a reaction in a gas at a constant pressure, then on the basis of the

45

Hess law the heat of reaction Q is equal to the difference in the enthalpies of the initial and final reaction products, i.e.,

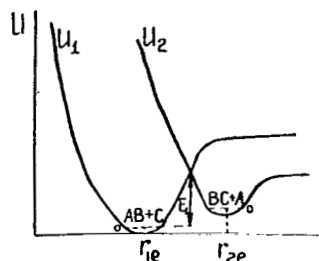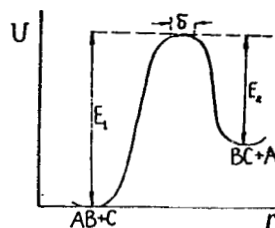$$Q_p = h_1 - h_2. \qquad (2.1.17)$$

Fig. 8   Fig. 9

Continuing the presentation of phenomenological chemical kinetics let us give some definitions.

1. We will always consider a reaction going from left to right, in accordance with (2.1.10), a forward reaction and we will use for its rate constant the generally accepted symbol k_f. For back reactions, going from right to left, k_b is the usual symbol for the rate constant.

2. In (2.1.11) the coefficients v'_j determine the order of a forward reaction with respect to the value j.

3. The following is the total order of a forward reaction

$$m' = \sum_{j=1}^{\mu} v'_j , \qquad (2.1.18)$$

the order of a back reaction is

$$m'' = \sum_{j=1}^{\mu} v''_j \qquad (2.1.19)$$

For example, for the reaction (2.1.I) the order of a forward re- action on the basis of oxygen O_2 is equal to one and is simultaneously the total order of a forward reaction. Along with a forward reaction there always occurs a reaction in the reverse direction. For the reaction (2.1.I) the back reaction is

$$O_2 \longleftarrow 2O. . \qquad (2.1.I')$$

Its order, as we can easily see, is two. If the formation rate R_α of the α-material is measured in mole/cm^3·sec then as follows from (2.1.11) the dimension of the rate constant is

$$[k_f] = (\text{mole})^{1-m'} (\text{cm}^3)^{m'-1} \text{ sec}^{-1}. \qquad (2.1.20)$$

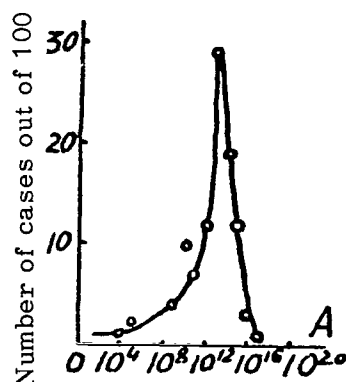Then from the total size of the rate constant it follows that for a monomolecular reaction ($m' = 1$, $k_f = Ae^{-E_0/RT}$) the dimension of the rate constant is the frequency (sec^{-1}). The values of A generally have an order of magnitude of $10^{12} - 10^{14}$ sec^{-1}. The following data which were gathered from a book by Kondrat'yev [19] give us an idea of how often the value of A has the above order. According to these data out of 100 cases in one case the value A has the order 10^4, in two 10^5, in four 10^9, in nine 10^{10}, in seven 10^{11}, in twelve 10^{12}, in twenty-nine 10^{13}, in nineteen 10^{14}, in twelve 10^{15}, in three 10^{16} and in one case 10^{17} sec^{-1} (Fig. 10). Thus, in the majority of cases (60 out of 100) the order of $10^{12} - 10^{14}$ is observed. In fact, the dissociation reactions of the type (2.1.I) are not monomolecular and go through two-body collisions. Reactions of the recombination type (2.1.I') are tri-molecular. Thus dissociation and recombination reactions take place in catalytic materials which may be molecules of different types. The rate of these reactions depends on the type of molecule which is the catalytic material. In the numerical calculations (see Chapter 3) for certain dissociation-type reactions for which we did not succeed in finding reaction rate constants in the litera-ture we applied a hypothesis about thermal dissociation (i.e., the reactions were considered monomolecular. The value of A in the calculations described above was assumed equal to 10^{13} sec^{-1}. The value of activation energy E_0 was assumed equal to the dissociation energy. This is true for unexcited molecules. /55
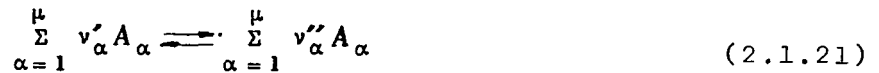

Fig. 10.

In Table 4 the rate constants for certain reactions are given.

TABLE 4

	Reactions	Catalytic material M	Rate constant, $cm^3 \cdot mole^{-1} \cdot sec^{-1}$
1	$O_2+M \rightarrow 2O+M$	O_2	$3.6 \cdot 10^{21} T^{-1/2} \cdot e^{-59380/T}$
		O	$2.1 \cdot 10^{18} T^{-1/2} \cdot e^{-59380/T}$
		N, N_2, NO	$1.2 \cdot 10^{21} T^{-1/2} \cdot e^{-59380/T}$
2	$N_2+M \rightarrow 2N+M$	N_2	$3 \cdot 10^{21} T^{-1/2} \cdot e^{-113260/T}$
		N	$1.5 \cdot 10^{22} T^{-1/2} \cdot e^{-113260/T}$
		O_2, O, NO	$9.9 \cdot 10^{20} T^{-1/2} \cdot e^{-113260/T}$
3	$NO+M \rightarrow N+O$	N_2, O_2, O, N, NO, Ar	$5.2 \cdot 10^{21} T^{-1/2} \cdot e^{-75490/T}$
4	$O_2+N \rightarrow NO+O$		$10^{12} T^{1/2} \cdot e^{-3120/T}$
5	$N_2+O \rightarrow NO+N$		$5 \cdot 10^{13} \cdot e^{-38000/T}$
6	$N_2+O_2 \rightarrow 2NO$		$9.1 \cdot 10^{24} T^{-1/2} \cdot e^{-65000/T}$
7	$NO^+ + e^- \rightarrow N+O$		$1.8 \cdot 10^{21} T^{-1/2}$

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As we already mentioned chemical reactions may occur both in a forward direction (reaction of initial materials with the formation of reaction products of a rate constant k_f) and in a back direction (reaction of reaction products with the formation of initial products of a rate constant k_b). The general form of the reaction

$$\sum_{\alpha=1}^{\mu} v'_\alpha A_\alpha \rightleftharpoons \sum_{\alpha=1}^{\mu} v''_\alpha A_\alpha \tag{2.1.21}$$

can also be written

$$\sum_{\alpha=1}^{\mu} v'_\alpha A_\alpha \xrightarrow{k_f} \sum_{\alpha=1}^{\mu} v''_\alpha A_\alpha; \tag{2.1.22}$$

$$\sum_{\alpha=1}^{\mu} v''_\alpha A_\alpha \xrightarrow{k_b} \sum_{\alpha=1}^{\mu} v'_\alpha A_\alpha. \tag{2.1.23}$$

For simultaneous chemical reactions the law of mass action (2.1.11) may be applied to each of the reactions (2.1.22) and (2.1.23), i.e.,

$$\bar{R}_\alpha = (v''_\alpha - v'_\alpha)k_f \prod_{j=1}^{\mu} w_j^{v'_j} + (v'_\alpha - v''_\alpha)k_b \prod_{j=1}^{\mu} w_j^{v''_j}. \tag{2.1.24}$$

In thermodynamic equilibrium there is no change in composition. Therefore, the constants k_f and k_b may be expressed by an equilibrium constant k_c. In fact,

$$R_\alpha = 0, \quad \frac{k_f}{k_R} = \prod_{j=1}^{\mu} w_j^{v''_j - v'_j} \equiv k_c. \tag{2.1.25}$$

The equilibrium constant k_c, as we know, may be calculated with great accuracy by methods of quantum mechanics and statistical physics. Sometimes it is more convenient to use the equilibrium constant expressed by partial pressures of the components. $p - w_\alpha RT$ and, therefore,

$$k_f/k_b = k_c = k_p (RT)^{-n}, \tag{2.1.26}$$

where

$$k_p = \prod_{j=1}^{\mu} (p_j)^{v''_j - v'_j}; \tag{2.1.27}$$

$$n = m'' - m'. \tag{2.1.28}$$

Generally an approximation of the function $k_p(T)$ in the form of a certain polynomial is used in numerical calculations.

Comprehensive information on the thermodynamic properties of materials (including information on equilibrium constants) is contained in [20].

Let us convert (2.1.24) using (2.1.27) and converting to mass concentrations:

$$\bar{R}_\alpha = (v''_\alpha - v'_\alpha) k_f \rho^{m'} \left(\prod_{j=1}^{\mu} \bar{c}_j^{v'_j} - \frac{1}{\dfrac{k_p}{p^n} \left(\sum_{\alpha=1}^{\mu} \bar{c}_\alpha \right)^n} \prod_{j=1}^{\mu} \bar{c}_j^{v''_j} \right).$$

(2.1.29)

Let there take place l reactions simultaneously in the gas mixture. Then the expression for the molar formation rate R_α of the α-material as a result of all the homogeneous reactions may be easily obtained by generalizing (2.1.29) for this case:

$$\bar{R}_\alpha = \sum_{r=1}^{l} (v''_{\alpha r} - v'_{\alpha r}) k_{fr} \rho^{m'_r} \left[\prod_{j=1}^{\mu} \bar{c}_j^{v'_{jr}} - \frac{1}{\dfrac{k_{pr}}{p^{n_r}} (\sum_\alpha \bar{c}_\alpha)^{n_r}} \prod_{j=1}^{\mu} \bar{c}_j^{v''_{jr}} \right],$$

(2.1.30) /57

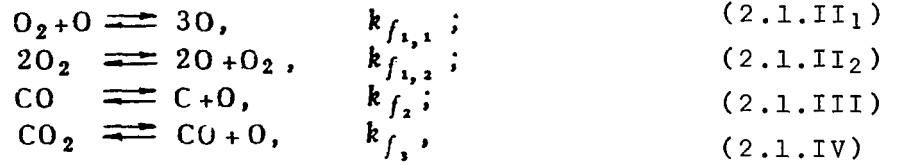here $v'_{\alpha r}$, $v''_{\alpha r}$ are the stoichiometric coefficients in the rth reaction ($r = 1,\ldots,l$),

$$\sum_{\alpha=1}^{\mu} v'_{\alpha r} A_\alpha \rightleftharpoons \sum_{\alpha=1}^{\mu} v''_{\alpha r} A_\alpha ,$$

(2.1.31)

$$m'_r = \sum_\alpha v'_{\alpha r}; \quad m''_r = \sum_\alpha v''_{\alpha r}; \quad n_r = m''_r - m'_r.$$

(2.1.32)

Thus, finally, the equations of continuity for the components (1.3.29), or as they are sometimes called, the equations of diffusion are written in the form

$$\frac{\partial \rho \bar{c}_\alpha}{\partial t} + \text{div}(\rho \bar{c}_\alpha \vec{v} + \vec{j}_\alpha) = \sum_{r=1}^{l} (v''_{\alpha r} - v'_{\alpha r}) k_{fr} \rho^{m'_r} \times$$

$$\times \left[\prod_{j=1}^{\mu} \bar{c}_j^{v'_{jr}} - \frac{1}{\dfrac{k_{pr}}{p^{n_r}} (\sum_\alpha \bar{c}_\alpha)^{n_r}} \prod_{j=1}^{\mu} \bar{c}_j^{v''_{jr}} \right].$$

(2.1.33)

Let us show by example how (2.1.33) is written for the special case. Let there be a gas mixture consisting of the components $C(N1)$, $CO(N2)$, $CO_2(N3)$, $O(N4)$, $O_2(N5)$ among which there occur the reactions

$$O_2 + O \rightleftharpoons 3O, \qquad k_{f_{1,1}}; \qquad\qquad (2.1.II_1)$$

$$2O_2 \rightleftharpoons 2O + O_2, \qquad k_{f_{1,2}}; \qquad\qquad (2.1.II_2)$$

$$CO \rightleftharpoons C + O, \qquad k_{f_2}; \qquad\qquad (2.1.III)$$

$$CO_2 \rightleftharpoons CO + O, \qquad k_{f_3}, \qquad\qquad (2.1.IV)$$

where $k_{f_{1.1}}$, $k_{f_{1.2}}$, k_{f_2} and k_{f_3} are the rates of forward reactions of $(2.1.II_1)$, $(2.1.II_2)$, $(2.1.III)$ and $(2.1.IV)$, respectively. For reaction $(2.1.II_1)$:

$$\left.\begin{array}{l} v'_1 = 0, \quad v'_2 = 0, \quad v'_3 = 0, \quad v'_4 = 1, \quad v'_5 = 1, \\ v''_1 = 0, \quad v''_2 = 0, \quad v''_3 = 0, \quad v''_4 = 3, \quad v''_5 = 0, \\ m' = 2, \quad m'' = 3, \quad n = 1. \end{array}\right\} \qquad (2.1.34)$$

For reaction $(2.1.II_2)$:

$$\left.\begin{array}{l} v'_1 = 0, \quad v'_2 = 0, \quad v'_3 = 0, \quad v'_4 = 0, \quad v'_5 = 2, \\ v''_1 = 0, \quad v''_2 = 0, \quad v''_3 = 0, \quad v''_4 = 2, \quad v''_5 = 1, \\ m' = 2, \quad m'' = 3, \quad n = 1. \quad \bullet \end{array}\right\} \qquad (2.1.35) \quad \underline{/58}$$

For the reaction $(2.1.III)$:

$$\left.\begin{array}{l} v'_1 = 0, \quad v'_2 = 1, \quad v'_3 = 0, \quad v'_4 = 0, \quad v'_5 = 0, \\ v''_1 = 1, \quad v''_2 = 0, \quad v''_3 = 0, \quad v''_4 = 1, \quad v''_5 = 0, \\ m' = 1, \quad m'' = 2, \quad n = 1. \end{array}\right\} \qquad (2.1.36)$$

For the reaction $(2.1.IV)$

$$\left.\begin{array}{l} v'_1 = 0, \quad v'_2 = 0, \quad v'_3 = 1, \quad v'_4 = 0, \quad v'_5 = 0, \\ v''_1 = 0, \quad v''_2 = 1, \quad v''_3 = 0, \quad v''_4 = 1, \quad v''_5 = 0, \\ m' = 1, \quad m'' = 2, \quad n = 1. \end{array}\right\} \qquad (2.1.37)$$
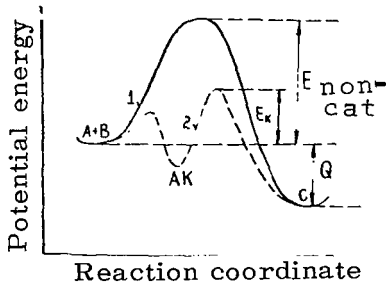
Fig. 11

Then, for example, for the O-component, the equation of diffusion is written as follows:

$$\frac{\partial \rho \bar{c}_4}{\partial t} + \operatorname{div}(\rho \bar{c}_4 \vec{v} + \vec{j}_4) = 2\rho^2 (k_{f_{1,1}} \bar{c}_4 + k_{f_{1,2}} \bar{c}_5)\left[\bar{c}_5 - \frac{\bar{c}_4^2}{\frac{k_p}{p}\sum_\alpha \bar{c}_\alpha}\right] + \qquad (2.1.38)$$

$$+ k_{f_2}\rho\left[\bar{c}_2 - \frac{\bar{c}_1 \bar{c}_4}{\frac{k_p}{p}\sum_\alpha c_\alpha}\right] + k_{f_3}\rho\left[\bar{c}_3 - \frac{\bar{c}_2 \bar{c}_4}{\frac{k_p}{p}\sum_\alpha c_\alpha}\right], \quad \alpha = 1,\ldots,5.$$

In conclusion let us note that in technology catalytic-type reactions are very important. The change in the chemical reaction rate under the effect of materials (catalysts) which do not appear in the final products of this reaction is called catalysis. Hence it follows that a homogeneous catalytic reaction goes through several elementary reactions in which the catalysts enters the reaction and is regenerated. If the catalyst accelerates the reaction this means that in the absence of a catalyst the reaction requires a great activation energy (E_{noncat} in Fig. 11).

Let there be a bimolecular reaction occurring in the absence of a catalyst according to the diagram

$$A + B \rightarrow C.$$

In the presence of an accelerating catalyst K the reaction goes through intermediate stages

$$A + K \rightleftharpoons AK;$$
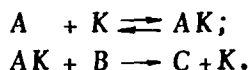$$AK + B \longrightarrow C + K.$$

Figure 11 shows the dependence of the potential energy system on the reaction coordinate in the absence of a catalyst (Curve 1) and with a catalyst (Curve 2).

Thus, to obtain correct results in studying the complex reactions we must apply (2.1.30) to each of the elementary stages through which the reaction in a system goes.

2. Chemically Frozen and Equilibrium Flows

The system of aerothermochemical equations (1.3.40)-(1.3.42) permits substantial simplifications in two extreme cases. Let us look at the equations of continuity for the components. They include terms which take into account the transition of the α-component across the surface of the elementary boundary in the gas phase and the formation of a component in it as a result of all the chemical reactions. When the macroscopic and microscopic transition of material is substantially greater than the formation of the component as a result of the chemical reactions we can disregard the right-hand sides of the equations of continuity and we come to equations of a chemically frozen flow. This case may be encountered at low temperatures or when the reaction rates are small as a result of the high activation energies. Thus, equations of diffusion for a frozen flow [9] are:

$$\frac{\partial}{\partial t} \rho c_\alpha + \text{div}(\rho c_\alpha \vec{v} + \vec{j}_\alpha) = 0, \quad \alpha = 1, \ldots, \mu. \qquad (2.2.1)$$

---

[9] Since we have agreed to study physically equilibrium flows, below in giving the theory of nonequilibrium flows we will not stipulate each time that we are speaking of chemical nonequilibrium (frozen, equilibrium) flows.

In the second extreme case (k_{fr}, $k_{br} \gg 1$) when the diffusive and convective transition of the material is substantially less than the formation of the component as a result of chemical reactions (high temperatures, relatively low activation energies) we come to a system of equations

$$\bar{R}_\alpha = 0 \qquad (2.2.2)$$

or in more detail:

$$\sum_{r=1}^{l} (v''_{\alpha r} - v'_{\alpha r}) \left[k_{fr} \rho^{m'_r} \prod_{j=1}^{\mu} \bar{c}_j^{v'_{jr}} - k_{br} \rho^{m''_r} \prod_{j=1}^{\mu} \bar{c}_j^{v''_{jr}} \right] = 0. \qquad (2.2.3)$$

Let us denote

$$v''_{\alpha r} - v'_{\alpha r} = a_{\alpha r}, \text{ and}$$

$$k_{fr} \rho^{m'_r} \prod_{j=1}^{\mu} \bar{c}_j^{v'_{jr}} - k_{br} \rho^{m''_r} \prod_{j=1}^{\mu} \bar{c}_j^{v''_{jr}} = x_r, \quad r = 1, \dots, l.$$

Then we can examine the system of equations (2.2.3) as a system of linear algebraic equations with constant coefficients and we can pose the question about its consistency. Thus,

$$\begin{cases} a_{11}x_1 + \dots + a_{1l} \, x_l = 0; \\ a_{\mu 1}x_1 + \dots + a_{\mu l} \, x_l = 0, \end{cases} \qquad (2.2.4)$$

Here l is the entire number of reactions including uniform reactions which occur in different catalytic materials. However, we can easily see that the number of unknowns can be reduced to k ($l = \sum_{r=1}^{k} n_r$ where n_r is the number of modifications of the reaction r). On the other hand, among μ equations not all are independent. In fact, ν linear relationships exist:

$$\sum_{\alpha=1}^{\mu} M_\tau n_{\tau\alpha} \bar{R}_\alpha = 0, \quad \tau = 1, \dots, \nu, \qquad (2.2.5)$$

which express the law of conservation of an element during chemical reactions (it is assumed that intranuclear conversions do not occur) and the equation of the conservation of mass is

$$\sum_{\alpha=1}^{\mu} M_\alpha \bar{R}_\alpha = 0. \qquad (2.2.6)$$

Equation (2.2.6), as we can easily see, is the result of ν preceding equations and, therefore, is not a new independent equation. Thus, we have $\mu - \nu$ independent equations for k unknowns. When the number of independent reactions is less than $\mu - \nu$, the task has been

formulated incorrectly. When $k = \mu - \nu$ the physical significance has only a trivial solution which leads to equations of detailed equilibrium. If $k > \mu - \nu$, generally from the total equilibrium there does not follow an equation of detailed equilibrium without applying new postulates which exceed the limits of the basic laws of thermodynamics. The repeatedly mentioned principle of the microscopic reversibility of Thomson [21,22] is such a principle whose special case is the principle of detailed equilibrium. According to this principle under equilibrium conditions the molecular process and the reverse process take place on the average at the same rate. For example, if the material in the gas phase is found in the three forms A, B, C among which mutual conversions occur then the total balance is not destroyed if the uniform motion in a cycle occurs (Fig. 12). The principle of microscopic reversibility asserts that equilibrium will be represented not by the cycle in Figure 12 but by the cycle in Figure 13. Thus, in a state of equilibrium each chemical reaction occurring in the system is self-balanced. When the principle of detailed equilibrium is not correct the concentration of all the components must experience vibrations in the approach to detailed equilibrium. Such studies were undertaken by Srabal [23] but they yielded no final results. Thus, for an equilibrium flow μ equations of diffusion are substituted by equations of continuity for a chemical element:

$$\frac{\partial}{\partial t} \rho \sum_{\alpha=1}^{\mu} \frac{n_{\tau\alpha} c_\alpha}{M_\alpha} + \mathrm{div} \sum_{\alpha=1}^{\mu} \frac{n_{\tau\alpha}}{M_\alpha} (\rho c_\alpha \vec{v} + \vec{j}_\alpha) = 0, \quad \tau = 1, \ldots, \nu, \qquad (2.2.7)$$
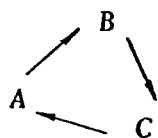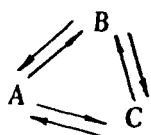

Fig. 12   Fig. 13

One of the equations of (2.2.7) can be substituted by

$$\sum_{\alpha=1}^{\mu} \bar{c}_\alpha M_\alpha = 1, \qquad (2.2.8)$$

and the $\mu - \nu$ independent equations for the equilibrium constant:

$$\prod_{j=1}^{\mu} \bar{c}_j^{\nu'_{jr}} = \frac{1}{\dfrac{k_{pr}}{p^{n_r}} \left(\displaystyle\sum_{\alpha=1}^{\mu} \bar{c}_\alpha \right)^{n_r}} \prod_{j=1}^{\mu} \bar{c}_j^{\nu''_{jr}}. \qquad (2.2.9)$$

3. Phase Equilibria in Single-Component Systems

The number of degrees of freedom in a single-component system is determined, as is known, by the formula

$$f = 3 - k \qquad (2.3.1)$$

where k is the number of phases. Thus a system consisting of one phase may have two degrees of freedom (e.g., pressure and temperature) a system of two phases may have one degree of freedom (pressure or volume or temperature) and finally if a system consists of three phases the number of degrees of freedom is equal to zero. This means that all three phases: liquid (L), gaseous (G) and solid (S) can exist only at one strictly defined pressure and temperature. A typical state diagram for such a system is represented in Figure 14.
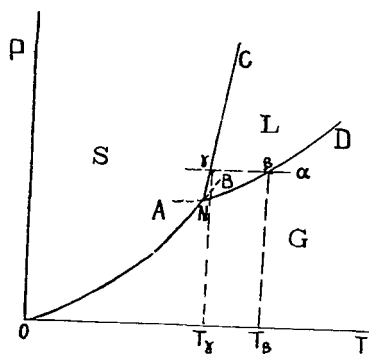

Fig. 14

Point N (the triple point of the phase diagram) represents those values of P and T at which three phases exist simultaneously. The sectors S, L and G represent the values of pressure and temperature at which only the solid, liquid or gaseous phase exists. The dividing lines are determined by the function $P(T)$ where the existence of two phases simultaneously is possible. In accordance with this, line ON is called the sublimation curve, line CN is the melting curve and line ND is the evaporation curve. Line ND ends at the critical point D. Let us note that with a slope of line NC to the right the volume of the materials converting from the solid to the liquid phase increases. For anomalous materials (gallium, water) the volume, on the contrary, decreases with a phase transition and the curve NC has a slope to the left. The dotted curves AN and BN represent metastable states. Let the pressure and temperature correspond to point α of the phase diagram. In this case the material is found only in the gaseous phase. If with a fixed pressure we decrease the temperature, moving to the left along the straight line $\alpha\gamma$ we will come to point β where there is the liquid phase. Subsequently the cooling of the liquid will occur while at point γ the solid phase will not appear. If the line $\alpha\gamma$ is drawn with a pressure $p = 1$ atm the point β is called the boiling point while the temperature corresponding to it T_β is the boiling temperature. Point γ is the melting point and T_γ is the melting temperature. For example, for graphite $\rho = 1 - 2.2$ g/cm^3 at $T = 20°C$, $c_p = 5.17$ cal/g·deg ($T = 1000°K$) and 7.9 cal/g·deg ($T = 2000°K$), $\kappa = 0.187$ cal/cm·sec·deg, $T_\gamma = 3772°K$, $T_\beta = 3927°K$ and $L = 14,132$ cal/g.

When the material is by-passed by the gas mixture in which the partial pressure of the vapors is less than the pressure of the saturated vapors at a temperature which corresponds to the temperature of the material, and when the temperature of the material is less than the temperature at the triple point of the phase diagram the material begins to sublimate. Let us look at the rate

of nonequilibrium evaporation from the surface of a material found in a solid or liquid state.

If the gas near the surface has a temperature T and a pressure p, the number of molecules colliding per unit area of surface is determined by the formula

$$n = Np/\sqrt{2\pi MRT}. \qquad (2.3.2)$$

If the Ath part of the molecules condenses [and the $(1-A)$th part is reflected] then obviously the number of condensed molecules is

$$n_{cond} = ANp/\sqrt{2\pi MRT}, \qquad (2.3.3)$$

where p is the pressure in dyn/cm^2 and R is the gas constant $(8.315 \cdot 10^7$ ergs/°K). If the vapor is saturated then per unit time more molecules are condensed than are evaporated, i.e.,

$$n_{evap} = ANp^*/\sqrt{2\pi MRT}, \qquad (2.3.4)$$

where p^* is the pressure of the saturated vapors of the surface material. Despite the external similarity of the formulas for n_{cond} and n_{evap} these values in essence do not have anything in common: n_{cond} is determined by the properties of the gas and n_{evap} depends on the energy necessary to overcome the intermolecular cohesive forces in the surface material. If the pressure $p \neq p^*$ the evaporation is nonequilibrium and, obviously, the mass velocity of carrying away the surface material U is determined by the formula (Hertz-Knudsen)

$$U = AM(p^* - p)/\sqrt{2\pi MRT}. \qquad (2.3.5)$$

The coefficient A is called the sticking probability and exerts a substantial influence on the evaporation rate, [24]. The value of A for the case of evaporation from a graphite surface is known with a very high degree of accuracy. Below we will give calculations of the chemically nonequilibrium boundary layer with the sticking probability changing in a range between 0.1 and 1. Shchennikov's paper [25] contains calculations of the equilibrium boundary layer with a wider interval of change in A (0.003-1.0).

We can easily obtain a differential equation for the phase equilibrium curve. As we know from thermodynamics, in the absence of gravitational, electrical and surface effects the Maxwell equation is satisfied

$$(\partial p/\partial T)_v = (\partial S/\partial v)_T, \qquad (2.3.6)$$

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where v, S are respectively the volume and entropy of the system. From experiments we know that in the processes of melting, evaporation and sublimation the change in the equilibrium pressure with temperature does not depend on the entire volume of the system. On the basis of the second law of thermodynamics the change in entropy with the phase transition $\Delta S = \Delta H/T = L/T$ where L is the heat of the phase transition. Thus,

$$dp/dT = L/T\Delta v,$$ (2.3.7)

Δv is the difference in molar volumes of the material in the two phases. Equation (2.3.7) is the known Clausius-Clapeyron equation. For the case of the processes of evaporation and sublimation (2.3.7) it is easy to integrate. In fact, in these processes the molar volume of the vapor is substantially more than the molar volume of the condensed phase (at moderate pressures):

$$v_{evap} >> v_{cond}$$

Therefore

$$\Delta v = v_{evap} - v_{cond} \sim v_{evap} = RT/p.$$ (2.3.8)

In addition,

$$L = L_0 + \int_0^T (\Delta c_p)dT,$$ (2.3.9)

here L_0 is the latent heat of transfer at 0°K which represents /65 the work which must be expended at absolute zero in order to tear molecules away from their neighbors in the condensed phase and to convert them to the gas phase. The second term in (2.3.9) represents the energy which must be transmitted to the system to compensate for the difference in the energies of thermal motion in the condensed phase and the gas. In the case of evaporation the basic part of the latent heat of transfer is usually represented by the first term in (2.3.9). Then (2.3.7) is converted to the form

$$d\ln p/dT = L_0/RT^2$$ (2.3.10)

and we can easily integrate it:

$$p^* = \text{const } e^{-L_0/RT}.$$ (2.3.11)

Thus, in this approximation it is enough to know the value of the equilibrium pressure of the vapors p^* at any one given temperature

in order to know it in an entire range of temperatures. Often it does not make sense to use more precise means of approximating $p*$
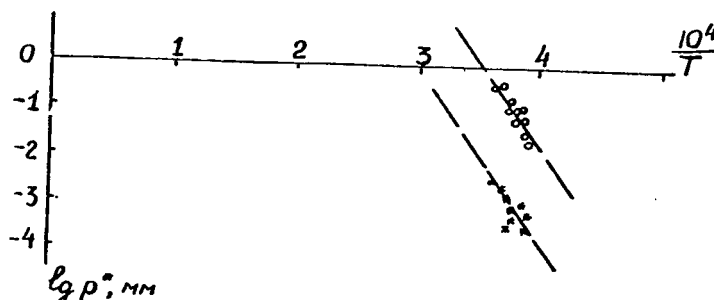

Fig. 15

(for example, by means of the Nernst equation $\lg p = A - \dfrac{B}{C} + cT + D\lg T$ as a result of the great discrepancies in experimental data with respect to the pressures of saturated vapors. For example, in 1952-1955 Goldfinger et al. measured the pressure of a saturated carbon vapor by a method of evaporation from an open surface (Langmuir method) and by the Knudsen effusion method [26]. There /66 was approximately a 100-fold difference in the data, but nevertheless at the present time they are assumed to be the most accurate [27] (see Fig. 15). Experimental data obtained on the basis of the Knudsen method are noted by the mark O and those obtained on the basis of the Langmuir method are marked by an *.

Below we will give numerical calculations of the boundary layer in which values of $p*$ were calculated according to experimental data obtained on the basis of both the Langmuir and Knudsen methods.

4. Kinetics of Heterogeneous Reactions

The phenomenon of surface destruction is complicated substantially if other heterogeneous processes» (catalytic or combustion-type) are possible on the surface. Thus, if a catalytic homogeneous reaction can be studied simply as a reaction occurring via several elementary reactions then any reaction on a solic surface can be subdivided at least into the following stages:
(1) Transfer of reacting materials to the surface;
(2) Chemical adsorption of reacting materials by the surface;
(3) Strictly chemical reaction of the surface between the adsorbed materials and the surface material or between the adsorbed material and the molecule colliding with the surface;
(4) Desorption of reaction products from the surface;
(5) Elimination of gaseous reaction products from the surface in the form of a convective current and be means of the diffusion mechanism. In addition, heterogeneous processes occur in the pores

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of the material, and it happens that the elimination mechanism of the formed components depends substantially on the radius of the pores. However, for studying aerothermochemical problems it is sufficient to take into account only the total effects caused by heterogeneous processes. For this purpose we can introduce the matrix ε of phenomenological coefficients as Rosner did [28]. The coefficients $\varepsilon_{ij}[i,j = 1,\ldots,\mu]$ of this matrix represent the probability of transition of the i-component as a result of adsorption, heterogeneous reactions and desorption into the j-component. Thus, the quadratic matrix ε with the dimension completely determines the local chemical activity of the surface. However, it is simpler to assume that the velocity U_α of the entry of the α-component into the gas phase as a result of all the heterogeneous processes is known (if $U_\alpha < 0$ it means that the α-component transfers at an absolute rate $|U_\alpha|$ from the gas to the condensed phase). Generally U_α must be determined experimentally.

1. *Adsorption*

Let us look briefly at certain features of heterogeneous processes on a surface. Two kinds of adsorption are known.

(1) Physical adsorption where molecules are retained on the surface at a distance of the order of 3Å by van der Waals forces which by nature are analogous to forces operating between the molecules in the gas;

(2) Chemical adsorption when adsorbed molecules are maintained at a distance of $\sim$ 1Å by forces of an atomic valent bond in the molecules. With chemisorption there can occur a decomposition of adsorbed molecules into atoms or radicals and an exchange of electrons with surface atoms. Generally in the overwhelming majority of cases the molecule colliding with the surface remains on it for a certain interval of time. Materials found in contact with cold (hot) air are warmed (cooled) mainly as a result of the adsorption mechanism. Langmuir developed a theory of adsorption based on the following assumptions:

(1) Molecules are adsorbed on definite segments of the adsorbent's surface. The number of adsorbing sites in the process does not change. The adsorbing sites are easily accessible and energetically equivalent.

(2) There is no physical reaction between the adsorbed molecules and as a result there is no molecular motion along the surface of the adsorbent.

(3) Molecules can be adsorbed only by colliding with the surface sites which are not already occupied by adsorbed molecules.

These three assumptions form the concept of the "ideal" adsorbed layer. Langmuir introduced the *first* supposition because

because molecules in a two-dimensional crystal lattice of the adsorbent's surface from a true alternation of potential maxima and minima. The second supposition is generally not true since adsorbed molecules almost always move along the surface. The third supposition automatically means that the adsorbed layer must be monomolecular. Let the number of molecules necessary for a complete surface coverage of all the adsorption centers for 1 cm^2 of surface be σ_0. Let us denote the number of adsorbed molecules of α-type per 1 cm^2 by σ_α. Thus, if per unit of time n_α, α-type molecules strike a unit surface area, then $n_\alpha \sum_{\beta=1}^{\mu} \sigma_\beta/\sigma_0$ of them returns to the gas phase and, therefore $n_\alpha(1- \sum_{\beta=1}^{\mu} \sigma_\beta/\sigma_0$ is adsorbed. Let τ_α be the mean time [10] during which the adsorbed α-type molecule remains on the surface. Then, obviously

$$\sigma_\alpha = \left(1 - \sum_{\beta=1}^{\mu} \sigma_\beta/\sigma_0\right) n_\alpha \tau_\alpha, \quad \alpha = 1, \ldots, \mu \qquad (2.4.1)$$

or

$$\theta_\alpha = n_\alpha \tau_\alpha \left(\sigma_0 + \sum_{\beta=1}^{\mu} n_\beta \tau_\beta\right)^{-1} \qquad (2.4.2)$$

where $\theta_\alpha = \sigma_\alpha/\sigma_0$ is the share of surface sites occupied by molecules of the α-component. Let θ_0 be the share of sites free for adsorption. Then, obviously,

$$\sum_\alpha \theta_\alpha + \theta_0 = 1. \qquad (2.4.3)$$

In addition, let us introduce the notation

$$n_\alpha \tau_\alpha / p_\alpha \sigma_0 = a_\alpha, \qquad (2.4.4)$$

where p is the partial pressure of the α-component and n_α is determined by the formula

$$n_\alpha = N p_\alpha / \sqrt{2\pi M_\alpha RT}. \qquad (2.4.5)$$

Then we can easily show that

$$\theta_0 = 1/(1 + \sum_\alpha a_\alpha p_\alpha), \qquad (2.4.6)$$

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[10] For example, for the adsorption of oxygen atoms on tungsten at 2548°K τ = 0.36 sec, at 2362°K, τ = 3.49 sec. Usually the dependence of the adsorption time on the surface temperature is approximated by the equation (of Frankel): $\tau = \tau_0 e^{q/RT}$, where τ_0 is the vibrational period of the adsorbed molecule in a direction perpendicular to the surface and q is the heat of adsorption.

and the equation of the Langmuir isotherm (2.4.2) becomes:

$$\theta_\alpha = a_\alpha p_\alpha \theta_0 .$$

(2.4.7)

Let us examine the energy equations with adsorption using a /69
hypothetical bivalent molecule as an adsorption sample [29]. In
Figure 16 the potential curve 1 refers to the physical adsorption
of the molecule AB. During chemical adsorption there is usually
dissociation into atoms. Curve 2 represents the dependence of the
potential energy of the system $A + B$ $[k]$ (where k is the surface
material) on the distance from the surface. The intersection of
curves 1 and 2 determines the value of the chemisorption activation
energy. In Figure 16, q_{phys} and q_{chem} are respectively the heats
of physical and chemical adsorption, E_α is the chemisorption
activation energy, E_{des} is the desorption activation energy and
Q_{AB} is the energy of the dissociation of molecules AB into atoms
$A + B$. Let us note the obvious relation

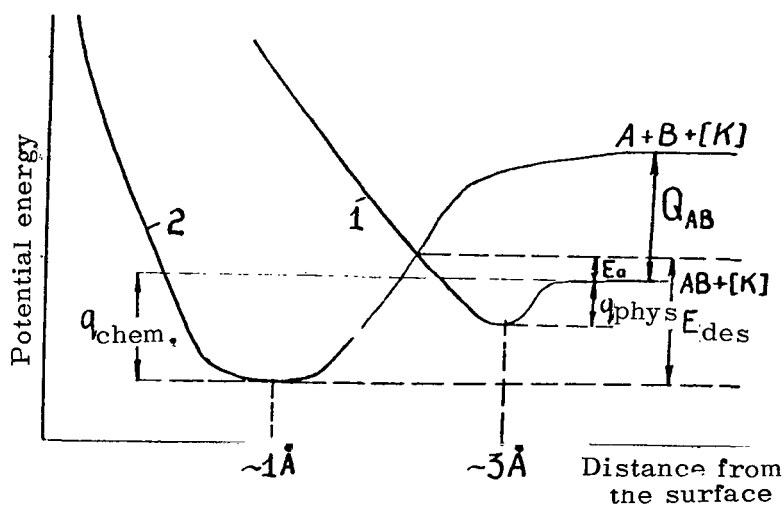$$E_{des} - E_\alpha = q_{chem}$$

(2.4.8)

Fig. 16

In Figure 16, the potential curves for illustrating exothermic
chemisorption are given. de-Boer indicated the possibility of
endothermic chemisorption. At high temperatures (in comparison
with chemisorption) the effect of physical adsorption on the
heterogeneous process is negligibly small. The activation energy
of physical adsorption is usually several kilocalories per mole.
The activation energy of chemisorption has the order of activation
energy of chemical reactions, for example, with the chemisorption
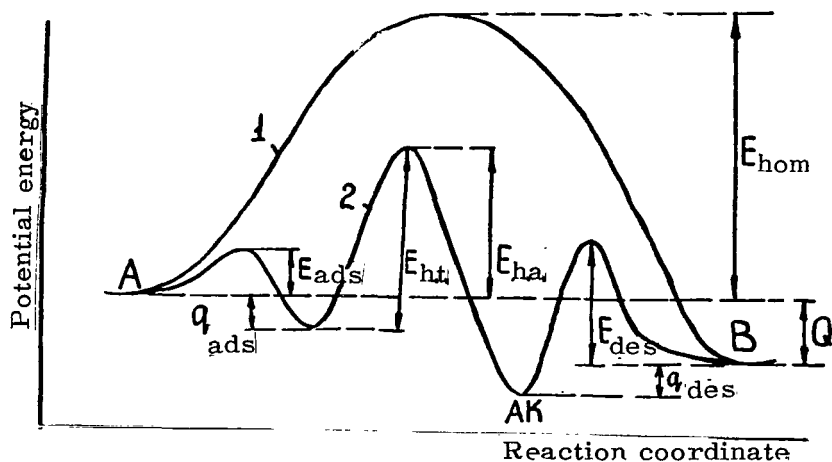of oxygen atoms on tungsten E_α = 147 kCal/mole.
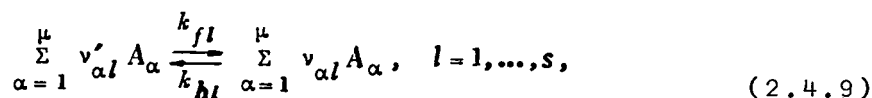
60

Fig. 17

2. Heterogeneous Catalysis

At the present time we assume that a catalyst participates at least in two stages of the overall process. During the process it subsequently enters the reaction and is regenerated. In this respect the position is the same as in homogeneous catalysis. The presence of a catalyst opens up a new path for the reaction which is made up of the abundance of elementary reactions in which the activation energy is substantially smaller than in a reaction without a catalyst. In Figure 17, we give a comparison of the profiles of a path of a homogeneous noncatalytic and a heterogeneous catalytic reaction $A \to B$. Curve 1 represents the homogeneous reaction and Curve 2 the heterogeneous reaction. In Figure 17 q_{ads}, q_{des} and Q are the heats of adsorption, desorption and the total heat of reaction; E_{ads}, E_{des}, E_{hom}, $E_{h.a.}$ and $E_{h,t}$ are respectively the activation energies of adsorption, desorption, homogeneous reaction and the apparent and true activation energies of the heterogeneous reaction. We can understand these values from Figure 17. As we know, a heterogeneous catalytic process can not displace equilibrium in the gas phase, otherwise this would contradict the second law of thermodynamics. A catalyst can not cause a reaction which under the given conditions is thermodynamically impossible. The activity of a catalyst in the process of changing the initial chemical system is not only an accelerating one but also an orienting one. The orienting activity of a catalyst is expressed only when the chemical system can be developed in several thermodynamically possible directions. Therefore, in the case of a catalytic surface there can not be detailed equilibrium on the surface. Only solid materials with a large bonding energy between atoms possesses catalytic activity. A large part of the catalysts possess ion or metallic crystal lattices with a large bonding energy [30]. In

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practice, cases of molecular crystals and liquids being heterogeneous catalysts are unknown. The overwhelming majority of catalysts are either metals or binary metal compounds or salts. Thus, using a general assumption about the catalytic surface must be considered in every case during the numerical calculations of aerothermochemical problems. Nevertheless in practical calculations, as a rule the assumption concerning detailed equilbrium on the surface of the material is applied since this substantially simplifies formulation of the problem.

The law of effective surfaces formulated by Langmuir is the basis for studying the kinetics of reactions in ideal adsorbed layers. According to the law of effective surfaces, for the reaction

$$\sum_{\alpha=1}^{\mu} v'_{\alpha l} A_{\alpha} \underset{k_{bl}}{\overset{k_{fl}}{\rightleftharpoons}} \sum_{\alpha=1}^{\mu} v_{\alpha l} A_{\alpha}, \quad l = 1, \dots, s,$$ (2.4.9)

occurring in the surface layer, the rate is proportional to the portions of the surface θ_{α} occupied by reacting materials in powers equal to the corresponding stoichiometric coefficients [cf. (2.1.30)]:

$$U_{\alpha} = \sum_{l=1}^{s} (v''_{\alpha l} - v'_{\alpha l}) \left[k_{fl} \prod_{\alpha=1}^{\mu} \theta_{\alpha}^{v'_{\alpha l}} - k_{bl} \prod_{\alpha=1}^{\mu} \theta_{\alpha}^{v''_{\alpha l}} \right] \theta_0^{n_l},$$ (2.4.10)

where $n_l = \sum_{\alpha=1}^{\mu} (v''_{\alpha l} - v'_{\alpha l})$, θ_0 is the portion of free sites of the surface. The degree of covering θ_{α} of the surface by the α-material is related to θ_0 by equations (2.4.7)

In the state of equilibrium $U_{\alpha} = 0$. Using the principle of microscopic reversibility and taking into account (2.4.7) we obtain

$$k'_{fl} / k'_{bl} = k_{pl} = \prod_{\alpha=1}^{\mu} p_{\alpha}^{v'_{\alpha}} \Big/ \prod_{\alpha=1}^{\mu} p_{\alpha}^{v''_{\alpha}}$$ (2.4.11)

where

$$k'_{fl} = k_{fl} \prod_{\alpha=1}^{\mu} a_{\alpha}^{v_{\alpha l}}, \quad k'_{bl} = k_{bl} \prod_{\alpha=1}^{\mu} a_{\alpha}^{v''_{\alpha l}}.$$ (2.4.12)

Thus, if the formation rate of the α-component ($\alpha = 1, \dots, \mu$), as a result of all the heterogeneous reactions, is equal to zero then from the equations for the ideal adsorption layer there result equations of detailed equilibrium.

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The law of effective surfaces occupies a place in the kinetics of heterogeneous catalytic reactions that is analogous to the place of the law of effective masses in the kinetics of homogeneous reactions. However if there is an interaction of adsorbed particles on the catalyst's surface and the number of active sites and their adsorptive capacity change during the course of the process itself the law of effective masses will not be satisfied. Therefore, the experimental study of the kinetics of heterogeneous processes on the surface of specific coatings is necessary.

3. Heterogeneous Combustion of a Graphite Surface

Bearing in mind the presentation of the numerical solutions of aerothermochemical equations for the case of the streamline flow of graphite by a high-enthalpy gas mixture let us study the heterogeneous combustion of graphite on the basis of experimental papers [31,32]. Experiments were performed up to a surface temperature of $\sim 2,000°K$. Below let us assume that: (1) sublimation and heterogeneous combustion reactions occur on the same active surface; (2) the reaction mechanism found by Blyholder [32] is preserved up to a surface temperature of $\sim 3,000°K$.

From Blyholder [32] it follows that the reaction rate does not depend on the degree of dissociation of O_2. Following the assumption of Moor and Zlotnik [16] let us assume that the adsorption of the O atom from CO_2 is still possible since the bonding energy of O in CO_2 is of the same order as in O_2 [33]. For simplicity let us assume that nitrogen and its compounds do not participate in heterogeneous reactions. Thus, the following irreversible combustion reactions and the sublimation reaction of the material are studied:

$$C_{graph.} \rightleftharpoons C_{gas}; \qquad (2.4.I)$$
$$C_{graph.} + O \longrightarrow CO; \qquad (2.4.II)$$
$$C_{graph.} + \tfrac{1}{2}O_2 \longrightarrow CO; \qquad (2.4.III)$$
$$C_{graph.} + CO_2 \longrightarrow 2CO. \qquad (2.4.IV)$$

The total number of O atoms per unit volume which can be adsorbed is /73

$$\rho\left(c_4 + \frac{M_4}{M_3}c_3 + c_5\right)\frac{N}{M_4} \qquad (2.4.13)$$

where N is Avogadro's number. The portion of these atoms necessary for O is $c_4/(c_4 + \frac{M_4}{M_3}c_3 + C_5)$, for O_2 $c_5/(c_4 + \frac{M_4}{M_3}c_3 + c_5)$ and for CO_2 $c_3\frac{M_4}{M_3}/(c_4 + \frac{M_4}{M_3}c_3 + c_5)$. Taking into account the fact that

desorption occurs only in the form of CO [32] we come to the conclusion that if ϕ is the number of carbon atoms desorbed per unit of time from a unit surface then ϕ gives the number of desorbed O atoms. Assuming a stationary state let us say that ϕ is the total number of O atoms adsorbed by the surface per unit of time per unit area. The value of ϕ is calculated by Blyholder [32] as:

$$\Phi = 1.55 \cdot 10^{11} \, T_w^{\frac{1}{2}} \, e^{-E/R \, T_w} \sqrt{k(n_4 + n_3 + 2n_5)}, \qquad (2.4.14)$$

where k is the Boltzmann constant and E is the activation energy (~ 2 kCal/mole). Then the mass velocity U_α of α-components entering the gas phase as a result of all the heterogeneous reactions is described by the following system of equations:

$$U_1 = U_{1\text{subl.}} \qquad (2.4.15)$$

$$U_2 = \Phi \frac{M_2}{N} + \frac{\frac{M_4}{M_3} c_3}{c_4 + c_5 + \frac{M_4}{M_3} c_3} \, \Phi \frac{M_2}{N}; \qquad (2.4.16)$$

$$U_3 = - \frac{\frac{M_4}{M_3} c_3}{c_4 + c_5 + \frac{M_4}{M_3} c_3} \, \Phi \frac{M_3}{N}, \qquad (2.4.17)$$

$$U_4 = - \frac{c_4}{c_4 + c_5 + \frac{M_4}{M_3} c_3} \, \Phi \frac{M_4}{N}; \qquad (2.4.18)$$

$$U_5 = - \frac{c_5}{c_4 + c_5 + \frac{M_4}{M_3} c_3} \, \Phi \frac{M_4}{N}. \qquad (2.4.19)$$

Here we have taken into account the fact that the adsorption of the /74 O atom from CO_2 leads to the formation of CO in the amount

$$\frac{\frac{M_4}{M_3} c_3}{c_4 + c_5 + \frac{M_4}{M_3} c_3} \, \Phi \frac{M_2}{N}. \qquad (2.4.20)$$

If we sum (2.4.15)-(2.4.19) we obtain the mass velocity of the removal of graphite from the surface which, as was to be expected, is equal to

$$\sum_{\alpha=1}^{5} U_\alpha = \cdot \Phi \frac{M_1}{N} + U_{1sub} \cdot$$

(2.4.21)

5. Heterogeneous Processes in Porous Surfaces

If the heat protective coating has a porous structure the reaction surface increases as a result of the internal reaction surface. However, if the porous granular structure in commercial catalysis permits an increase in the escape of the product a porous structure of the coating is undesirable. This is because the carrying away of the mass of the porous coating would be substantially more than the loss of mass by a solid coating with an insignificant supplementary absorption by the material.

Let us introduce the following symbols [34]: s_g is the surface area of the pores per 1 g; V_g is the volume of the pores per 1 g; ρ_t is the chemical density of the material and ρ_p is the density of the sample.

The share of the total volume of a material devoted to pores is called the porosity of a porous material. If V is the volume of 1 g of the sample, the porosity θ is

$$\theta = V_p / V.$$

(2.5.1)

Since

$$V_p = \frac{1}{\rho_p} - \frac{1}{\rho_t},$$

(2.5.2)

then

$$\theta = (\rho_t - \rho_p)/\rho_t \cdot$$

(2.5.3)

Porous materials may possess anisotropy (e.g., wood) and also an organized structure (e.g., a correct stacking up of spheres) or disorganized structure of pores. Below we will refer to isotropic material.

We can easily show that the surface area of a porous material /75 consists of pore holes for portion θ and of solid material for portion $(1-\theta)$. In fact, let there be a sample of unit length and unit cross section (1 cm^2). The sample will have a unit volume and, by definition the volume of all the pores will equal θ. Let us assume that the sample is cut into thin sections each having a width of Δx. All the sections will have statistically the same overall area of entrance pore holes which we shall symbolize by A_p. Then the volume for the pores in each thin section is $A_p\Delta x$ and the total volume of the pores of the sample is A_p, but this is the porosity θ, i.e., $A_p = \theta$.

We can roughly estimate the mean radius of the pores $\bar{r}$ if we

assume that pores are one unbroken cylinder of circular cross section.

$$\bar{r} = 2V_g/S_g .$$

(2.5.4)

For activated carbon S_g = 500 - 1500 m^2/g, V_g = 0.6 - 0.8 cm^3/g and therefore $\bar{r}$ = 20 Å. For commercial catalysts (e.g., vanadium used in the process of obtaining sulfur gas) $\bar{r}$ can reach 2000 Å. The total length of the pores for 1 g of material is estimated from the equation

$$L_g = S_g^2/4\pi V_g .$$

(2.5.5)

For a material for which $S_g \sim 1,000$ m^2/g and $V_g \sim 0.7$ cm^3/g L_g is 10^{13} cm. Pores can be communicating or uncommunicating. Obviously the gas flow in pores is possible even if part of the pores communicate among themselves and with the surface of the material. This part of the pores forms the active pore space. Therefore we can generally introduce two porosities, the total θ and the active θ_α which is the ratio of the volume of the pores communicating among themselves to the total volume of the material. Certain volcanic rocks have a high total porosity but a small active porosity.

Keeping in mind a study of the flow of a chemically reacting gas in the pores let us introduce the length $L_{p\alpha}$ of the pores at which an equilibrium value of the concentration of the α-component is established as a result of heterogeneous reactions. Then $S_{p\alpha}$ (the reaction surface area per 1 cm^2 of the material's surface) is estimated from the equation

$$S_{p\alpha} = 2\pi \bar{r} n_p L_{p\alpha} ,$$

(2.5.6)

where n_p is the number of escapes of the pores per 1 cm^2 of the materials surface. If we assume that a pore is a circular cylinder perpendicular to the surface of the material, then obviously,

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$$n_p = \theta/\pi\bar{r}^2 .$$

(2.5.7)

We can introduce the simplest correction to (2.5.7) for the dip angle of the cylinder to the surface since the mean statistical dip angle is $\sim$ 45°. Thus,

$$n_p = \theta/\pi\bar{r}^2\sqrt{2}.$$

(2.5.8)

Semi-empirically instead of $1/\sqrt{2}$ the correction coefficient $\theta^{1/2}$ or $\theta^{1/3}$ is obtained. But since $\theta \sim 0.5$ for the majority of materials the correction obtained is unimportant. We can easily see that n_p for θ = 0.5 and $\bar{r}$ = 10 Å is $\sim 10^{13}$ cm^{-2}. Taking (2.5.8) into account, equation (2.5.6) is converted to the form

$$S_{p\alpha} = \theta\sqrt{2}L_{p\alpha}/\bar{r}.$$

(2.5.9)

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If $L_{p\alpha} \sim 5\mu$ then $S_{p\alpha} \sim 10^3$. Thus, in such case the outer reaction surface is $\sim$ 0.1% of the total reaction surface. During the molecular motion of initial materials in the pores of the material their concentration must in general diminish as a result of collisions with the pore walls (since part of such collisions leads to the reaction) with a growth in the concentration of reaction products. The value of the drop in concentration depends substantially on the reaction rates, diffusion coefficients and the dimensions of the pores. Depending on the radius of the pores the nature of the diffusion in them may be different. If the dimensions of the pores are small in comparison with the mean free path of the λ molecules then during their motion there will occur frequent collisions with the walls and infrequent collisions with each other. When the mean free path of the molecules is small in comparison with the dimensions of the pores $2\bar{r}$, the molecules will undergo frequent collisions with each other and infrequent collisions with the pore walls. Thus, in the first case ($2\bar{r}/\lambda \ll 1$) the flow in the pores will be a free molecular one and in the second extreme case ($2\bar{r}/\lambda \gg 1$) a hydrodynamic description of the flow is necessary. As we know the mean free path of molecules is

$$\lambda = k T / p \pi \sigma^2 \sqrt{2},$$
(2.5.10)

where p is the pressure and σ is the diameter of the molecules. $\underline{/77}$
Assuming that $T \sim 2,000^\circ K$, $\bar{r} \sim 10\text{Å}$ and $\sigma \sim 4\text{Å}$ we find that in the pores there will exist a free molecular flow up to a pressure of the order of several hundreds of atmospheres, i.e., in all cases of practical interest. Below in our numerical calculations we will limit ourselves to a study of the first extreme case ($2\bar{r}/\lambda \ll 1$). In studying this case it is natural to apply the Knudsen theory concerning free molecular flow in an infinite tube. Knudsen obtained the following expression for the coefficient of diffusion of the α-component (see, for example [35,21].

$$D_\alpha = \frac{2\bar{r}}{3} \sqrt{\frac{8 k T}{\pi m_\alpha}}$$
(2.5.11)

As we can easily see the coefficient of diffusion D_α does not depend on the presence of other types of molecules. In obtaining (2.5.11) it was assumed that:
    (1) The tube has an infinite length;
    (2) The walls completely scatter the molecules in accordance with the Knudsen law. This law says that the number of molecules tearing away from the surface in a definite direction is proportional to the cosine of the angle between this direction and the normal to the surface;
    (3) The gas is found in equilibrium and conforms to the Maxwell distribution.

    The first two assumptions permit obvious refinements, for example by taking into account a certain part of the molecules

which are reflected by the wall like a mirror. As for the last as-
sumption it is clear that the gas in the flow is found under condi-
tions which are far from those of equilibrium. This follows from
the fact that such an equilibrium can be retained by a large number
of molecular collisions. However, in a free molecular flow the num-
ber of collisions between molecules is insignificant, but since other
data are lacking let us assume that the third assumption is satisfied.

Let us look at the elementary volume in a pore (Fig. 18). The
difference in the diffusion currents of the α-component through the
cross section y and $y + dy$ is equal to the formation rate Z_α of the
α-component as a result of all the heterogeneous reactions on the
surface of the pores:

$$m_\alpha \pi \bar{r}^2 D_\alpha n_\alpha'' dy = -2\pi \bar{r}(1-\theta) Z_\alpha dy \qquad (\alpha = 1, ..., \mu),$$

(2.5.12)

where n_α is the density of the number of particles of the α-component
in the pores and the derivative is taken in the direction y.
Boundary conditions for equations (2.5.12) are:

Fig. 18

$$y = 0, \qquad n_\alpha = n_{\alpha w};$$ (2.5.13)
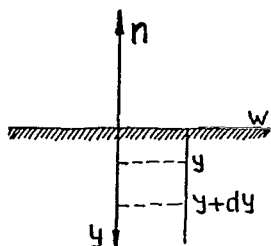$$y = L, \qquad n_\alpha' = 0,$$ (2.5.14)

where L is the mean statistical depth of pores con-
nected to the surface. The second boundary condition
(2.5.14) follows from the condition of non-flowing
trough the solid wall. We will assume that at dis-
ances of the order $L p_\alpha$ we can disregard the change
of temperature in the material so that the coeffi-
cient of diffusion D_α does not depend on y. Otherwise we would have
to add the equation of thermal conductivity to the system of equa-
tions (2.5.12). In the right-hand side of equations (2.5.12) the simp-
lest correction was made for the internal structure of the pores in
such a way that we are limited to the study of flow theory in pores
in a one-dimensional arrangement. Integrating (2.5.12) once and using
(2.5.14) we obtain the escape velocity $U_{\alpha p}$ of the α-component
from the pores:

$$U_{\alpha p} = \pi \bar{r}^2 n_p D_\alpha m_\alpha n_\alpha' = 2\pi \bar{r} n_p (1-\theta) \int_0^L Z_\alpha dy.$$

(2.5.15)

Summing (2.5.15) over α we obtain the amount of substance of
the material which enters the gas phase per unit of time from a
unit area of the pores:

$$U_p = 2\pi \bar{r} n_p (1-\theta) \int_0^L \sum_{\alpha=1}^\mu Z_\alpha dy.$$

(2.5.16)

the mean statistical depth of the pores must be determined exper-
imentally. However, if the value L is unknown, it is permissible

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to replace the upper limit of the integration in the integrals of the equations (2.5.15) and (2.5.16) by ∞ if $L_{p\alpha} < L$.

Note 1. Let the true reaction rate be of the order of m and the activation energy E. The gas escape velocity from the pores is determined by the equation

$$\pi \bar{r}^2 D \frac{dn}{dy} = -2\pi \bar{r} ke^{-E/RT} \int_{y=0}^{y=L} n^m dy.$$
(2.5.17)

The boundary conditions are: $n = n_w$ at $y = 0$ and $n = 0$ at $y = L$. Then the mean concentration gradient is $-n_w/L$. The mean concentration value in the pore is $\sim n_w/2$. Using these simplifications, we obtain from (2.5.17)

$$\pi \bar{r}^2 D \frac{n_w}{L} = 2\pi \bar{r} k_f e^{-E/RT} \frac{n_w^m}{2^m} L,$$
(2.5.18)

whence

$$L = 2^{\frac{m-1}{2}} \sqrt{\bar{r} D/k_f e^{-E/RT} n_w^{m-1}}.$$
(2.5.19) /79

Substituting (2.5.19) in the left-hand and right-hand side of (2.5.18) we obtain a formula for evaluating the apparent reaction rate

$$U \sim \frac{\pi \bar{r}}{2^{\frac{m-1}{2}}} \sqrt{\bar{r} k_f e^{-E/RT} D n^{m+1}}.$$
(2.5.20)

Thus, the apparent reaction rate has an order of $\frac{m+1}{2}$ and the apparent activation energy is 1/2 of the true activation energy.

Note 2. Let us examine the evaporation through the pores of the material. If we assume that the evaporation mechanism in the pores of the material is described by the Hertz-Knudsen formula for nonequilibrium evaporation, then as follows from the above, the flow in the pores is described by the equation

$$\bar{r} D n'' = -\frac{A(p_1^* - knT)}{\sqrt{2\pi mkT}} 2(1-\theta).$$
(2.5.21)

The boundary conditions: $y = 0$, $n = n_w$; $y = L$, $dn/dy = 0$.

Equation (2.5.21) is easily integrated on the assumption that $T = T_w = $ const. If we assume that $\bar{r} << L$, the form of the Hertz-Knudsen formula is retained completely:

$$U_p = A_{eff} (p_1^* - nkT)/\sqrt{2\pi mkT}.$$
(2.5.22)

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However, equation (2.5.22) includes the effective sticking probability which is related in the following way to the sticking probability of A for a nonporous surface:

$$A_{eff} = [(1-\theta) + 2\theta\sqrt{2(1-\theta)/3A}]A.$$
(2.5.23)

Formula (2.5.22) is not valid for very large porosities. This is because of the very simple way of taking into account the internal structure of the pores by introducing a correction factor $(1 - \theta)$ for the internal effective surface. As we can easily see, (2.5.23) gives a substantial correction for small values of A and in addition we note that A_{eff} can be greater than unity. The necessity of taking into account evaporation from the material's pores may /80 be one of the reasons for the discrepancy between values of the sticking probabilities obtained in the experiments.

Note 3. Let us give equations which describe the flow of a gas in graphite pores in the absence of sublimation. In writing the equations the results of experiments from [31,32] (see Section 4, Chapter 2) were used.
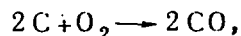
$$\overline{r} D_\alpha n_\alpha'' = 2(1-\theta)\frac{n_\alpha \Phi}{n_3 + n_4 + 2n_5}, \qquad \alpha = 3, 4, 5;$$
(2.5.24)

$$\overline{r} D_2 n_2'' = -2(1-\theta)\frac{2n_3 + n_4 + 2n_5}{n_3 + n_4 + 2n_5}\Phi.$$
(2.5.25)

The carrying away of the mass of the material through the pores:

$$U_p = 2\pi \overline{r}(1-\theta)m_1 n_p \int_0^\infty \Phi dy.$$
(2.5.26)

Note 4. Let only one reaction occur in the surface pores, for example

$$2C + O_2 \longrightarrow 2CO,$$

while the general form of the differential equation which describes the flow of the gas in a pore is:

$$n_\alpha'' = f(n_\alpha).$$
(2.5.27)

Equation (2.5.27) can be integrated once:

$$n_\alpha' = \left[2\int_0^{n_\alpha} f(n_\alpha)\,dn_\alpha + A\right]^{1/2},$$
(2.5.28)

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where A is the integration constant. If we assume that with $y = L$, not only $n'_\alpha = 0$ but $n_\alpha = 0$, then

$$n'_\alpha = \sqrt{2} \left[\int_0^{n_\alpha} f(n_\alpha) \, dn_\alpha \right]^{1/2} . \qquad (2.5.29)$$

The escape of O_2 atoms through a zero cross section of the pores will be:

$$U_5 = -n_p \pi \bar{r}^2 \left(\frac{dn_5}{dy} \right)_{y=0} , \qquad (2.5.30)$$

and the escape velocity of the CO atoms (and therefore C) through the pores will be:

$$U_1 = -2n_p \pi \bar{r}^2 \left(\frac{dn_5}{dy} \right)_{y=0} \qquad (2.5.31)$$

Using (2.4.14) in the form /81

$$\Phi = 1.55 \cdot 10^{11} T_w^{3/4} e^{-E/RT_w} \sqrt{2kn_5} \qquad (2.5.32)$$

and (2.5.29) we obtain

$$U_1 = 1.4 \cdot 10^{-4} N\theta (1-\theta)^{1/2} T_w^{1/4} e^{-E/2RT_w} p_e^{1/4} (\bar{c}_{5w} / \Sigma_\alpha \bar{c}_\alpha)^{1/4} . \qquad (2.5.33)$$

Comment on Chapter 2

If the experimental data with respect to the rate constants k_{br} ($r = 1,\ldots,l$) of back chemical reactions are known, the formation rate of the α-component as a result of all the homogeneous reactions must be determined from the formula [cf. (2.1.29)]:

$$\bar{K}_\alpha = \sum_{r=1}^{l} (v''_{\alpha r} - v'_{\alpha r}) \left[\rho^{m'_r} k_{fr} \prod_{j=1}^{\mu} \bar{c}_j^{v'_{jr}} - \rho^{m''_r} k_{br} \prod_{j=1}^{\mu} \bar{c}_j^{v''_{jr}} \right], \quad \alpha = 1, \ldots, \mu .$$

The law of effective masses $k_{br} = k_{fr}/k_{cr}$ is generally correct for a reacting gas mixture found close to chemical equilibrium.

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CHAPTER 3

NUMERICAL SOLUTIONS TO AEROTHERMOCHEMICAL EQUATIONS

1. Boundary Layer Equations

Let us look at the stationary flow of a chemically nonequilibrium gas in the boundary layer on an axisymmetric body. We may obtain boundary layer equations in the usual way on the basis of the Prandtl method [22,36] if we assume that $\delta \ll R$, where δ is the thickness of the boundary layer and R is the radius of curvature of the generatrix of the body.

The equation of continuity:

$$\frac{\partial}{\partial s} \rho u r^k + \frac{\partial}{\partial y} \rho v r^k = 0.$$

(3.1.1)

The equation of momentum:

$$\rho u \frac{\partial u}{\partial s} + \rho v \frac{\partial u}{\partial n} = -\frac{\partial p}{\partial s} + \frac{\partial}{\partial n}\left(\eta \frac{\partial u}{\partial n}\right).$$

(3.1.2)

The equation of continuity for the components:

$$\rho u \frac{\partial \bar{c}_\alpha}{\partial s} + \rho v \frac{\partial \bar{c}_\alpha}{\partial n} + \frac{\partial \bar{j}_{\alpha n}}{\partial n} =$$
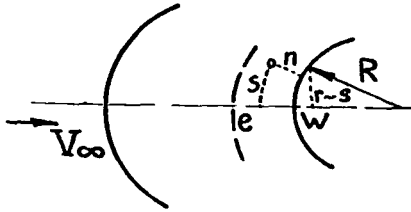
(3.1.3)

$$= \sum_{r=1}^{l} (v''_{\alpha r} - v'_{\alpha r})\left[k_{fr} \rho^{m'_r} \cdot \prod_{j=1}^{\mu} \bar{c}_j^{v'_{jr}} - k_{br} \rho^{m''_r} \prod_{j=1}^{\mu} \bar{c}_j^{v''_{jr}} \right].$$

The equation of energy:

$$\rho u \frac{\partial}{\partial s} \sum_{\alpha=1}^{\mu} \bar{c}_\alpha M_\alpha h_\alpha + \rho v \frac{\partial}{\partial n} \sum_{\alpha=1}^{\mu} \bar{c}_\alpha M_\alpha h_\alpha =$$

(3.1.4)

$$= u \frac{dp}{ds} + \eta \left(\frac{\partial u}{\partial n}\right)^2 + \frac{\partial}{\partial n} \varkappa \frac{\partial T}{\partial n} - \frac{\partial}{\partial n} \sum_{\alpha=1}^{\mu} \bar{j}_\alpha M_\alpha h_\alpha.$$

The equation of state:

$$p = \rho R T \sum_{\alpha=1}^{\mu} \overline{c}_\alpha . \qquad (3.1.5)$$

Here the coordinates s and n pertain to generatrix of the body (Fig. 19); $k = 0$ for flat bodies and $k = 1$ for bodies of rotation. Bearing in mind the study of axisymmetric flows let us apply the Dorodnitsyn transform in the Liz form to equations (3.1.1) – (3.1.5)

Fig. 19

$$\lambda = \frac{r u_e}{\sqrt{2\xi}} \int_{n=0}^{n} \rho \, dn ; \qquad \xi = \int_{s=0}^{s} \rho_w \eta_w u_e r^2 ds \qquad (3.1.6)$$

and let us introduce the following dimensionless functions:

$$f = \psi / \sqrt{2\xi}; \quad \overline{I}_{\alpha\lambda} = \overline{j}_{\alpha n} \rho / \lambda_n \rho_w \eta_w; \quad H = M_k h / R T_e; \quad \gamma = c_p M_k / R$$

$$\lambda_n = \partial\lambda/\partial n = r \rho u_e / \sqrt{2\xi}; \quad h = \sum_{\alpha=1}^{\mu} c_\alpha h_\alpha,$$

where Ψ is the flow function determined from (3.1.1) and M_k is the molecular weight of one of the components whose choice is arbitrary. Then

$$\rho v = -\frac{1}{r} [(\sqrt{2\xi} f_\xi + f/\sqrt{2\xi})\xi_s + \sqrt{2\xi} f_\lambda \lambda_s]; \qquad (3.1.7)$$

$$(l f_{\lambda\lambda})_\lambda + f f_{\lambda\lambda} + 2 \left(\frac{\rho_e}{\rho} - f_\lambda^2\right) \frac{d \ln u_e}{d \ln \xi} = 2\xi [f_\lambda f_{\lambda\xi} - f_\xi f_{\lambda\lambda}]; \qquad (3.1.8)$$

$$\left(\frac{\gamma l}{\Pr} t_\lambda\right)_\lambda + t_\lambda \left[f \gamma - \frac{M_k}{R} \sum_{\alpha=1}^{\mu} c_{p\alpha} \overline{I}_{\alpha\lambda} M_\alpha\right] - \sum_{\alpha=1}^{\mu} H_\alpha M_\alpha [(\overline{I}_{\alpha\lambda})_\lambda - f \overline{c}_{\alpha\lambda}] =$$

$$= 2\xi \left[f_\lambda \left(H_\xi + \frac{M_k}{R T_e} \frac{\rho_e}{\rho} u_e u_{e\xi}\right) - f_\xi H_\lambda\right] - u_e^2 f_{\lambda\lambda}^2 \frac{M_k}{R T_e} l; \qquad (3.1.9)$$

$$(\overline{I}_{\alpha\lambda})_\lambda - f \overline{c}_{\alpha\lambda} + 2\xi [f_\lambda \overline{c}_{\alpha\xi} - f_\xi \overline{c}_{\alpha\lambda}] = \overline{R}_\alpha \frac{2\xi}{\rho u_e \xi_s}, \quad \alpha = 1, ..., \mu . \qquad (3.1.10) \quad \underline{/84}$$

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In the vicinity of the critical point the system (3.1.7) - (c.1.10) reduces to the form

$$\rho v = -f\sqrt{2\rho_w \eta_w u_{es}};\qquad(3.1.11)$$

$$(lf_{\lambda\lambda})_\lambda + ff_{\lambda\lambda} + \frac{1}{2}\left(\frac{\rho_e}{\rho} - f_\lambda^2\right) = 0;\qquad(3.1.12)$$

$$\left(\frac{\gamma l}{\Pr}t_\lambda\right)_\lambda + t_\lambda\left[f\gamma - \frac{M_k}{R}\sum_{\alpha=1}^{\mu}c_{p\alpha}\bar{I}_{\alpha\lambda}M_\alpha\right] = \sum_{\alpha=1}^{\mu}H_\alpha M_\alpha[(\bar{I}_{\alpha\lambda})_\lambda - f\bar{c}_{\alpha\lambda}];\qquad(3.1.13)$$

$$(\bar{I}_{\alpha\lambda})_\lambda - f\bar{c}_{\alpha\lambda} =$$

$$= \frac{1}{2u_{es}}\sum_{r=1}^{l}(v''_{\alpha r} - v'_{\alpha r})\rho^{m'_r - 1}\left[k_{fr}\prod_{j=1}^{\mu}\bar{c}_j^{v'_{jr}} - \rho^{n_r - 1}k_{br}\prod_{j=1}^{\mu}\bar{c}_j^{v''_{jr}}\right].\qquad(3.1.14)$$

Let us give another equation of continuity for the elements:

$$\sum_{\alpha=1}^{\mu}n_{\tau\alpha}[(\bar{I}_{\alpha\lambda})_\lambda - f\bar{c}_{\alpha\lambda}] = 0,\quad \tau = 1,\dots,\nu,\quad \alpha = 1,\dots,\mu.\qquad(3.1.15)$$

In the case of "frozen" boundary layer (see chapter 2, section 2) we can disregard the right-hand sides of the equations of diffusion (3.1.10) and (3.1.14). Thus,

$$(lf_{\lambda\lambda})_\lambda + ff_{\lambda\lambda} + 2\left(\frac{\rho_e}{\rho} - f_\lambda^2\right)\frac{d\ln u_e}{d\ln\xi} = 2\xi[f_\lambda f_{\lambda\xi} - f_\xi f_{\lambda\lambda}].\qquad(3.1.16)$$

$$\left(\frac{\gamma l}{\Pr}t_\lambda\right)_\lambda + t_\lambda\left[f\gamma - \frac{M_k}{R}\sum_{\alpha=1}^{\mu}c_{p\alpha}\bar{I}_{\alpha\lambda}M_\alpha\right] - \sum_{\alpha=1}^{\mu}H_\alpha M_\alpha[(\bar{I}_{\alpha\lambda})_\lambda - f\bar{c}_{\alpha\lambda}] =$$

$$= 2\xi\left[f_\lambda\left(\frac{\rho_e}{\rho}u_e u_{e\xi}\frac{M_k}{RT_e} + H_\xi\right) - f_\xi H_\lambda\right] - u_e^2 f_{\lambda\lambda}^2\frac{M_k}{RT_e}l;\qquad(3.1.17)$$

$$(\bar{I}_{\alpha\lambda})_\lambda - f\bar{c}_{\alpha\lambda} = 2\xi[f_\xi\bar{c}_{\alpha\lambda} - f_\lambda\bar{c}_{\alpha\xi}],\quad \alpha = 1,\dots,\mu.\qquad(3.1.18)$$

At the critical point of the axisymmetric body:

$$(lf_{\lambda\lambda})_\lambda + ff_{\lambda\lambda} + \frac{1}{2}\left(\frac{\rho_e}{\rho} - f_\lambda^2\right) = 0;\qquad(3.1.19)$$

$$\left(\frac{\gamma l}{\Pr}t_\lambda\right)_\lambda + t_\lambda\left[f\gamma - \frac{M_k}{R}\sum_{\alpha=1}^{\mu}c_{p\alpha}\bar{I}_{\alpha\lambda}M_\alpha\right] = 0;\qquad(3.1.20)$$

$$(\bar{I}_{\alpha\lambda})_\lambda - f\bar{c}_{\alpha\lambda} = 0,\quad \alpha = 1,\dots,\mu.\qquad(3.1.21)$$

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In the second extreme case of an "equilibrium" boundary layer
(chapter 2, section 2) we obtain:

$$(lf_{\lambda\lambda})_\lambda + ff_{\lambda\lambda} + 2\left(\frac{\rho_e}{\rho} - f_\lambda^2\right)\frac{d\ln u_e}{d\ln \xi} = 2\xi[f_\lambda f_{\lambda\xi} - f_\xi f_{\lambda\lambda}]; \tag{3.1.22}$$

$$\left(\frac{\gamma l}{\Pr}t_\lambda\right)_\lambda + t_\lambda\left[f\gamma - \frac{M_k}{R}\overset{\mu}{\underset{\alpha=1}{\Sigma}}c_{p\alpha}\bar{I}_{\alpha\lambda}M_\alpha\right] - \overset{\mu}{\underset{\alpha=1}{\Sigma}}H_\alpha M_\alpha[(\bar{I}_{\alpha\lambda})_\lambda - f\bar{c}_{\alpha\lambda}] =$$

$$= 2\xi\left[f_\lambda\left(H_\xi + \frac{M_k}{RT_e}\frac{\rho_e}{\rho}u_e u_{e\xi}\right) - f_\xi H_\lambda\right] - u_e^2 f_{\lambda\lambda}^2\frac{M_k}{RT_e}l; \tag{3.1.23}$$

$$f\overset{\mu}{\underset{\alpha=1}{\Sigma}}n_{\tau\alpha}\bar{c}_{\alpha\lambda} - \overset{\mu}{\underset{\alpha=1}{\Sigma}}n_{\tau\alpha}(\bar{I}_{\alpha\lambda})_\lambda = 2\xi(f_\lambda\overset{\mu}{\underset{\alpha=1}{\Sigma}}n_{\tau\alpha}\bar{c}_{\alpha\xi} -$$

$$- f_\xi\overset{\mu}{\underset{\alpha=1}{\Sigma}}n_{\tau\alpha}\bar{c}_{\alpha\lambda}), \quad \tau = 1,\ldots,\nu-1; \tag{3.1.24}$$

$$\overset{\mu}{\underset{\alpha=1}{\Sigma}}M_\alpha\bar{c}_\alpha = 1; \tag{3.1.25}$$

$$\overset{\mu}{\underset{j=1}{\Pi}}\bar{c}_j^{\nu'_{jr}} = \frac{1}{\dfrac{k_{pr}}{p_e^{n_r}}\left(\overset{\mu}{\underset{\alpha=1}{\Sigma}}\bar{c}_\alpha\right)^{n_r}}\overset{\mu}{\underset{j=1}{\Pi}}\bar{c}_j^{\nu''_{jr}} \tag{3.1.26}$$

At the critical point of the body:

$$(lf_{\lambda\lambda})_\lambda + ff_{\lambda\lambda} + \frac{1}{2}\left(\frac{\rho_e}{\rho} - f_\lambda^2\right) = 0; \tag{3.1.27}$$

$$\left(\frac{\gamma l}{\Pr}t_\lambda\right)_\lambda + t_\lambda\left[f\gamma - \frac{M_k}{R}\overset{\mu}{\underset{\alpha=1}{\Sigma}}c_{p\alpha}\bar{I}_{\alpha\lambda}M_\alpha\right] = \overset{\mu}{\underset{\alpha=1}{\Sigma}}H_\alpha M_\alpha[(\bar{I}_{\alpha\lambda})_\lambda - f\bar{c}_{\alpha\lambda}]; \tag{3.1.28}$$

$$f\overset{\mu}{\underset{\alpha=1}{\Sigma}}n_{\tau\alpha}\bar{c}_{\alpha\lambda} - \overset{\mu}{\underset{\alpha=1}{\Sigma}}n_{\tau\alpha}(\bar{I}_{\alpha\lambda})_\lambda = 0, \quad \tau = 1,\ldots,\nu-1; \tag{3.1.29}$$

$$\overset{\mu}{\underset{\alpha=1}{\Sigma}}M_\alpha\bar{c}_\alpha = 1; \tag{3.1.30}$$

$$\frac{k_{pr}}{p_e^{n_r}}\left(\overset{\mu}{\underset{\alpha=1}{\Sigma}}\bar{c}_\alpha\right)^{n_r}\overset{\mu}{\underset{j=1}{\Pi}}\bar{c}_j^{\nu'_{jr}} = \overset{\mu}{\underset{j=1}{\Pi}}\bar{c}_j^{\nu''_{jr}}. \tag{3.1.31}$$

2. Boundary Conditions

The boundary conditions of a problem on the surface of a
strong break can be obtained in two ways: either by integrating

the equations of continuity, motion and energy over the boundary encompassing the surface of the body and by subsequent contraction of the boundary (as was done, for example, in [37,38,25]) or by writing an equation of balance. It is understood that the final results obtained by the first or second method coincide. We will give the derivation of the boundary conditions by the second method in which the physical sense of each of the equation's terms is clearly evident.

Let us look at the boundary which includes the surface of the body. Then the carrying away of energy from the boundary as a result of diffusion, radiation and convection is compensated by the supply of energy as a result of the thermal conductivity and by the entry of the mass of the body with a specific energy suitable for the energy of the body. Let us disregard the heat flux into the body and let us also not take into account the radiant heat flux from the hot gases to the surface which is evidently considerable only at very high temperatures (see, for example, the work of Keck et al [39] on the emission radiation of the air). Below, for the sake of simplicity, we will assume that the body consists of one element to which we can apply the index 1. Contracting the boundary let us obtain

$$\varkappa \frac{\partial T}{\partial n} = \sum_{\alpha=1}^{\mu} c_\alpha h_\alpha (\rho v)_+ + \sum_{\alpha=1}^{\mu} h_\alpha j_{\alpha n} + \varepsilon\sigma T_w^4 - (\rho v)_- \varphi, \qquad (3.2.1)$$

where (ρv) is the amount of the substance of the body which enters the boundary per unit of time across a unit area.

Let us study the balance of the mass. The amount of the α-component carried away from the boundary as a result of convection and diffusion is equal to the amount R_α of the component which enters the boundary as a result of desorption from the surface of the body plus the amount of the α-component formed in the boundary as a result of all the homogeneous reactions:

$$j_\alpha d\sigma + (\rho v)_+ c_\alpha d\sigma = R_\alpha dv + U_\alpha d\sigma. \qquad (3.2.2)$$

Contracting the boundary and taking into account the fact that the term $R_\alpha dv$ is a value of the highest order of smallness we obtain .

$$j_\alpha + (\rho v)_+ c_\alpha = U_\alpha, \qquad \alpha = 1, ..., \mu. \qquad (3.2.3)$$

The smallness of the term $R_\alpha dv$ in comparison with the other terms means that if a state of detailed chemical equilibrium is possible on the surface of the body then it is achieved as a result of heterogeneous rather than homogeneous reactions. But in an equilibrium boundary layer (see Chapter 2, Section 2) the state of detailed equilibrium which is reached as a result of the rapid flow of reactions in the gas phase is extrapolated right up to the surface of the body. From the mathematical point of view this is due to the

discarding of the differential parts of $\mu-\nu$ equations of continuity for the components and their conversion into final equations.

Summing (3.2.3) over α from 1 to μ, we obtain

$$(\rho v)_+ = \sum_{\alpha=1}^{\mu} U_\alpha = (\rho v)_-. \tag{3.2.4}$$

We can easily see that, in the first method of obtaining boundary conditions, (3.2.4) is found by integrating the equation of continuity over the boundary. In integrating (3.2.4) we used the physically evident equations

$$\sum_{\alpha=1}^{\mu} j_\alpha = 0; \qquad \sum_{\alpha=1}^{\mu} \bar{c}_\alpha M_\alpha = 1.$$

Taking into account (3.2.3) and (3.2.4) let us simplify (3.2.1):

$$\varkappa \frac{\partial T}{\partial n} + \sum_{\alpha=1}^{\mu} U_\alpha(\varphi - h_\alpha) = \varepsilon \sigma T_w^4. \tag{3.2.5}$$

Let us look at the system s of heterogeneous reactions of the type:

$$\sum_{\alpha=1}^{\mu} \nu_{\alpha l} A_\alpha + B_1 \rightleftharpoons \sum_{\alpha=1}^{\mu} \nu''_{\alpha l} A_\alpha, \tag{3.2.6}$$
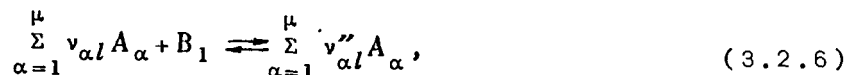
where B_1 is the solid phase component and A_α is the gas phase component. In a stationary case the desorption rate of the A_α-component is equal to its formation rate as a result of all the heterogeneous reactions. Then

$$\sum_{\alpha=1}^{\mu} U_\alpha(\varphi - h_\alpha) = \sum_{l=1}^{s} \sum_{\alpha=1}^{\mu} U_{\alpha l}(\varphi - h_\alpha) = \tag{3.2.7}$$

$$= \sum_{l=1}^{s} U_{1l} \sum_{\alpha=1}^{\mu} (\nu''_{\alpha l} - \nu'_{\alpha l})(\varphi - h_\alpha) = \sum_{l=1}^{s} U_{1l} Q_l,$$

Here $U_{\alpha l}$ is the formation rate of the α-component in the lth heter- ogeneous reaction, U_{1l} is the combustion rate of the B_1-component in the lth reaction and Q_l is its heat. Thus the equation of energy balance is written:

$$\varkappa \frac{\partial T}{\partial n} + \sum_{l=1}^{s} U_{1l} Q_l = \varepsilon \sigma T_w^4. \tag{3.2.8}$$

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1. Sublimation of the Material in the Absence of Other Heterogeneous Processes

Let us look at a case of the sublimation of a body on whose surface there are no other heterogeneous processes. Thus the following reaction takes place on the surface of the body

$$B_1 \rightleftharpoons A_1 \qquad (3.2.9)$$

(for a body made of graphite this is $C_{graphite} \rightleftharpoons C_{gas}$). Equation (3.2.8) is simplified:

$$\varkappa \frac{\partial T}{\partial n} - (\rho v)_- \, L = \varepsilon \sigma T_w^4, \qquad (3.2.10)$$

where L is the sublimation energy (see Chapter 2, Section 3). Below in numerical calculations of the boundary layer on a graphite surface the heat of transfer was assumed to be constant; for carbon its value was taken as 171 kcal/mole in accordance with the recommendation given in the book by Nesmeyanov [27]. Such a value for L was found by Melvin-Kh'yuz [40] after studying the heats of reaction. To complete the system of equations and boundary conditions, as we know, we need one more condition for the evaporation rate. The Hertz-Knudsen formula for nonequilibrium can be this condition:

$$(\rho v)_- = \frac{A M_1}{\sqrt{2\pi M_1 R T_w}} \left[p_1^* - p_e \frac{\bar{c}_{1w}}{\sum\limits_{\alpha=1}^{\mu} \bar{c}_\alpha} \right] \qquad (3.2.11)$$

In the vicinity of the critical point in the Dorodnitsyn variables the boundary conditions for a sublimating body, on whose surface there are no other heterogeneous processes, are written in the form

$$\bar{c}_1 = \frac{1}{M_1} + \frac{\bar{I}_{1\lambda}}{f} ; \qquad (3.2.12)$$

$$\bar{c}_\alpha = \bar{I}_{\alpha\lambda}/f; \qquad (3.2.13)$$

$$f \frac{L}{T_e R} + \frac{\gamma}{Pr} t_\lambda - \frac{\varepsilon \sigma T_w^4}{T_e R \sqrt{2\rho_w \eta_w u_{es}}} = 0; \qquad (3.2.14)$$

$$f = -\frac{A M_1}{\sqrt{4\pi M_1 R T_w u_{es} \rho_w \eta_w}} \left[p_1^* - p_e \frac{\bar{c}_{1w}}{\sum\limits_{\alpha=1}^{\mu} \bar{c}_{\alpha w}} \right] \qquad (3.2.15)$$

Note. If as a result of chemical reactions in the gas phase the A_1-component transfers to the composition of other components at a great rate so that c_{1w} is near zero, i.e., $p_1 \ll p_1^*$ then

(3.2.15) is simplified:

$$f = - \frac{A M_1 p_1^*}{\sqrt{4\pi M_1 R T_w u_{es} \rho_w \eta_w}} \cdot \qquad (3.2.16)$$

In the second extreme case when $p_1 \sim p_1^*$ the equation (3.2.15) is replaced by

$$p_1 = p_1^* \cdot \qquad (3.2.17)$$

In this case in the numerical calculations the carrying away of the mass is determined from the equation of energy and the temperature is determined from (3.2.17). Satisfying (3.2.17) means physically that the evaporation rate is so great that despite the escape of the A_1 - component as a result of convection, diffusion and chemical reactions the vapor pressure of the A_1-component is close to the saturation pressure.

2. Catalytic Surface

For a stationary, pure catalysis the following equation must be satisfied (see Chapter 2, Section 4, Subsection 2)

$$\sum_{\alpha=1}^{\mu} U_\alpha = 0. \qquad (3.2.18)$$

The following reaction scheme represents the frozen boundary layer: /90 reactions localized on the surface of the gas-solid body section. The gas phase is only a resevoir for molecules entering the hetero-geneous reactions and for molecules formed during the reactions. In an equilibrium boundary layer we assume that the equilibrium reached on the surface as a result of heterogeneous catalytic re-actions is preserved in the gas phase as a result of the action of homogeneous reactions occurring at a high rate. The system of equations (3.2.3) permits an investigation that is analogous to the investigation of transfer to the frozen and equilibrium boun-dary layer (Section 2, Chapter 2). When the mass transfer as a result of convection and diffusion is substantially more than the formation rate of the component as a result of heterogeneous pro-cesses, the equations are satisfied:

$$j_\alpha + \rho v c_\alpha = 0, \quad \alpha = 1, ..., \mu, \qquad (3.2.19)$$

which we can call boundary conditions for a chemically inert and impervious surface. In the opposite extreme case

$$U_\alpha = 0, \quad \alpha = 1, ..., \mu. \qquad (3.2.20)$$

As follows from what we have described earlier (Chapter 2, Section 4, Subsection 2) equations of detailed equilibrium result from

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(3.2.20) for an ideal adsorbed layer. For catalytic reactions the equation of energy balance is simplified:

$$\kappa \frac{\partial T}{\partial n} = \sum_{\alpha=1}^{\mu} U_\alpha h_\alpha + \varepsilon \sigma T_w^4 .$$

(3.2.21)

At will we can write the balance of energy via heats of reactions as we did in (3.2.8).

3. Boundary Conditions for a Body Made of Graphite

Using the results from Chapter 2, Section 4, Subsection 3, we can easily obtain boundary conditions for a case of the streamline flow of a graphite surface by a high-enthalpy gas mixture.

The balance of mass on the surface:

$$j_1 + \rho v c_1 = U_{1\,\text{subl}} .$$

(3.2.22)

$$j_\alpha + \rho v c_\alpha = U_\alpha \qquad (\alpha = 2, \ldots, 5),$$

(3.2.23)

where U_α is the α-component's rate of entering the gas phase and values of U_α are determined from equations (2.4.15) - (2.4.19). Summing (3.2.22) and (3.2.23) and converting to the Dorodnitsyn /91 variables we obtain a condition for the mass rate of evaporation at the critical point of an axisymmetric body:

$$f = -\frac{AM_1\left(p_1^* - p_e \dfrac{\bar{c}_1}{\sum\limits_{\alpha=1}^{\mu} c_\alpha}\right)}{\sqrt{4\pi M_1 R T_w}\,\rho_w \eta_w u_{es}} - \frac{M_1 \Phi}{N\sqrt{2\rho_w \eta_w u_{es}}} .$$

(3.2.24)

The equation of energy:

$$\frac{\gamma}{\Pr} t_\lambda - \frac{M_1 \varepsilon \sigma T_w^4}{T_e R \sqrt{2\rho_w \eta_w u_{es}}} - \frac{f_{1c} Q_c}{T_e R} - \frac{1}{T_e R} \sum_{l=2}^{4} f_{1l} Q_l = 0,$$

(3.2.25)

where

$$f_{1c} = -AM_1\left(p_1^* - p_e \frac{\bar{c}_1}{\sum\limits_{\alpha=1}^{\mu} \bar{c}_\alpha}\right)\bigg/ \sqrt{4\pi M_1 R T_w \rho_w \eta_w u_{es}};$$

(3.2.26)

$$f_{1l} = -U_{1l}\big/\sqrt{2\rho_w \eta_w u_{es}}$$

(3.2.27)

Q_c and Q_l are the heats of the following reactions:

$$C_{graphite} \rightleftharpoons C_{gas}; \tag{3.2.I}$$

$$C_{graphite} + O \rightleftharpoons CO; \tag{3.2.II}$$

$$C_{graphite} + \tfrac{1}{2}O_2 \rightleftharpoons CO; \tag{3.2.III}$$

$$C_{graphite} + CO_2 \rightarrow 2CO. \tag{3.2.IV}$$

We can easily see that the equation of mass and energy balance includes terms which take into account the effect of sublimation and other heterogeneous reactions in such a way that the effect of both carrying-away mechanisms has been divided. Since the pressure of saturated vapors depends very strongly on temperature (this law is close to the exponential law) then from evaluation it follows that the effect of sublimation becomes predominant only at surface temperatures of $\sim$ 3,000°K. In the case of sufficiently low surface temperatures ($\sim$ 2,000°K) we can assume that the boundary conditions depend only on the rates of heterogeneous reactions:

$$f = -M_1 \Phi / N \sqrt{2\rho_w \eta_w u_{es}}; \tag{3.2.28}$$

$$\frac{\gamma}{Pr} t_\lambda - \frac{M_1 \varepsilon \sigma T_w^4}{T_e R \sqrt{2\rho_w \eta_w u_{es}}} - \frac{1}{T_e R} \sum_{l=2}^{4} f_{1l} Q_l = 0. \tag{3.2.29}$$

Note: We can easily generalize the obtained expressions for /92 boundary layers on the surface of a body for a case when the body is a mechanical mixture of different substances B_s. To do this it is sufficient to introduce the value $\phi_s = P_s/P$ which is the share of the surface occupied by the substance B_s. Obviously if the escape of the substance B_s from a unit of the surface is $(\rho v)_s$, the entire escape is

$$\rho v = \sum_{s} (\rho v)_s \varphi_s. \tag{3.2.30}$$

4. Boundary Conditions Taking into Account Reactions in the Pores of the Body.

Using the results from Chapter 2, Section 5, as in Subsection 1 in the same assumptions, let us write the balance of energy on the surface of the body:

$$\varkappa \frac{\partial T}{\partial n} = \sum_{\alpha=1}^{\mu} c_\alpha h_\alpha (\rho v)_+ + \sum_{\alpha=1}^{\mu} h_\alpha j_{\alpha n} + \varepsilon \sigma T_w^4 - [U_T + U_p] \varphi, \tag{3.2.31}$$

where U_T is the rate of the carrying away of the mass of the body from the solid surface. Let us look at the mass balance. The

amount of the α-component carried away from the boundary (which covers the surface of the body) as a result of convection and diffusion is equal to the amount of the component entering the boundary as a result of desorption from a solid surface and from the pores of the body. Contracting the boundary, we obtain

$$j_\alpha + (\rho v)_+ c_\alpha = U_\alpha, \quad \alpha = 1, \ldots, \mu,$$
(3.2.32)

where

$$U_\alpha = U_{\alpha p} + U_{\alpha T}.$$
(3.2.33)

Summing (3.2.33) over α we obtain an expression for the total carrying away of the mass:
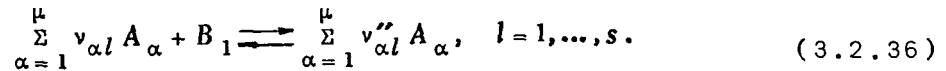
$$(\rho v)_+ = U_p + U_T,$$
(3.2.34)

where U_p is determined from (2.5.16). Multiplying (3.2.32) by h_α, summing over α and substituting in (3.2.31) we have

$$\varkappa \frac{\partial T}{\partial n} = \varepsilon \sigma T_w^4 + \sum_{\alpha=1}^{\mu} U_\alpha (h_\alpha - \varphi).$$
(3.2.35)

As we can easily see the external form of (3.2.3) and (3.2.5) coincides with the external form of (3.2.32) and (3.2.35). The only difference is in writing the equations for U_α.

Let us look at the system s of heterogeneous reactions /93

$$\sum_{\alpha=1}^{\mu} v_{\alpha l} A_\alpha + B_1 \rightleftharpoons \sum_{\alpha=1}^{\mu} v_{\alpha l}'' A_\alpha, \quad l = 1, \ldots, s.$$
(3.2.36)

We can easily show that in this case the equation of energy balance reduces to the form

$$\varkappa \frac{\partial T}{\partial n} = \varepsilon \sigma T_w^4 - (1-\theta) \sum_{l=1}^{s} Z_{1l} Q_l - 2\pi \bar{r} (1-\theta) n_p \sum_{l=1}^{s} Q_l \int_0^L Z_{1l} dy,$$
(3.2.37)

where Z_{1l} is the combustion rate of the B_1-component in the lth heterogeneous reaction. The second term in the right-hand side of (3.2.37) pertains to the carrying away of the mass of the B_1 component of the solid phase as a result of heterogeneous reactions on the outer side of the body. In many cases we can disregard this term in comparison with the last term of the right-hand side of the equation which takes into account the final reaction rates in the pores of the body. In addition, if $L_{p\alpha} < L$ then the upper limit of integration may be replaced by ∞ (see Chapter 2, Section 5). In this case the equation of energy balance is simplified:

$$\varkappa \frac{\partial T}{\partial n} = \varepsilon \sigma T_w^4 - 2\pi \bar{r} (1-\theta) n_p \sum_{l=1}^{s} Q_l \int_0^\infty Z_{1l} dy.$$
(3.2.38)

Note: Generally the sticking probability $f_\lambda = 0$ is given for the equation of motion on the surface. However, if in addition to the solid and gaseous phases there is also a liquid phase then we must know the velocity of the melt's surface. It is generally assumed that the profile of the velocity of the melt u is linear:

$$u = cn. \tag{3.2.39}$$

Here the coefficient c is determined by the viscosity of the melt. The temperature profile in the melt is also generally assumed to be linear. If we solve the steady-state problem, then the thickness of the melt δ is a given value. Writing the other boundary conditions at the boundaries of the section gas-melt, melt solid phase is done in the usual way as we did it above. Unsteady melting of a viscous material is studied, for example, in the work by Paskonov and Polezhayev [41].

5. *Conditions at the Outer Limit of a Boundary Layer*

Conditions at the outer limit of a boundary layer must be obtained by solving a nonequilibrium problem

$$t = 1, \quad f_\lambda = 1, \quad \bar{c}_\alpha = \bar{c}_{\alpha e}.$$

For part of the numerical calculations we did not arrange the data on the basis of a solution of an outer equilibrium problem. In these cases the state at the outer limit of a boundary layer was assumed to be equilibrium. In this case μ conditions $\bar{c}_\alpha = \bar{c}_{\alpha l}$ are replaced by $\mu - \nu$ independent equations, $\nu - 1$ conditions of the conservation of the element and $\sum\limits_{\alpha=1}^{\mu} \bar{c}_\alpha M_\alpha = 1$ The method for calculating the concentrations at a constant pressure is included in the work by Gurevich and Shaulov [42]. Let us note that recently calculations were made of the supersonic streamline flow of blunt materials by an entirely nonequilibrium dissociated gas at varied parameters of an oncoming current. In the papers by Velotserkovskiy and Dushin [43] and Lun'kin and Popov [44] calculations were made on the basis of the Dorodnitsyn method for calculating nonequilibrium dissociated oxygen. Accurate calculations of precisely this kind must yield boundary conditions for solving boundary layer equations. We used the data from the paper by Lun'kin and Popov [44] to make numerical calculations of a chemically nonequilibrium boundary layer along the generatrix of the body of rotation.

3. Calculations of the Streamline Boundary Layer with Chemical Reactions in the Vicinity of the Critical Point of the Body of Rotation

As we have already mentioned all the calculations were made on a sample of graphite heat protective coating. As a rule,

graphite is not used as a heat protective material, mainly due to the fact that its thermal conductivity coefficient has a substantially higher value than it has in other coatings [45]. Nevertheless, it is important to study the destruction of graphite in a flow of high-temperature gas if only because its percentage is great in many heat protective coatings. In addition the combustion of carbon was studied more completely by experiments than other materials although the study of the mechanism of heterogeneous processes on the surface of carbon is far from complete. The carrying away of a mass of graphite as a result of erosion (as we know from experimental data) is substantially less than the carrying away of the mass as a result of sublimation and heterogeneous combustion. Thus, a heat protective coating made only of carbon is a very convenient model for a theoretical investigation.

The basic purposes for the numerical calculations made on an /95 an electronic computer were:

(1) To calculate the chemically nonequilibrium boundary layer for a case of the streamline flow of graphite by oxygen;

(2) To compare existing calculations in the limits of a frozen and equilibrium boundary layer with calculations made taking into account the final rate of the chemical reactions occurring in a gas, on the surface and in the pores of the body;

(3) To study the effect of various molecular models on the mass velocity of the carrying away of the substance of a body and the distribution of concentrations, etc.;

(4) To study the effect of the inaccuracy of our information concerning the pressure of saturated carbon vapors on the values which characterize the destruction of the coating.

All the cases studied pertain to the streamline flow of a body which repeats its form during decomposition.

As follows from what we have given above aerothermochemical equations are very complex and usually do not permit analytical investigation. Therefore the method of mathematical modeling on computers becomes the basic method for calculating the effect of any boundary layer parameter . Calculations were performed in such a way that on the whole one of the boundary layer parameters changed while the others remained fixed. In all we made 30 calculations of the streamline flow of an axisymmetric body in the vicinity of the critical point. The res   of the calculations are given in Table 5. All the calculations, except No. 9, were made for the case of the streamline flow of graphite by oxygen. Calculation No. 9 represents the streamline flow of graphite by air. Boundary layer parameters for which the calculations were performed, are given in Table 5. We will not recalculate their value for each individual calculation; let us note only that $u_{es} = 2,200$ sec^{-1} represents the

TABLE 5

No. of calculation	Type of layer	Molecular reaction represents the model	R,m	P_e,atm	A	ε
1.	Frozen	Lennard-Jones	1	0.981	0.1	0
2.	Nonequilibrium	"	"	"	"	"
3.	"	"	"	"	"	"
4.	Frozen	"	"	"	"	"
5.	Equilibrium	Solid Spheres	"	"	"	"
6.	Nonequilibrium	"	"	"	"	"
7.	Frozen	"	"	"	"	"
8.	Nonequilibrium taking into account the final heterogeneous reaction rate	"	"	"	"	"
9.	Frozen	"	"	"	"	"
10.	"	"	"	1.07	0.082	"
11.	Nonequilibrium	"	"	"	"	"
12.	"	"	"	10	0.1	"
13.	Frozen	"	"	"	"	"
14.	Nonequilibrium	"	4	0.981	"	"
15.	Frozen	"	"	"	"	"
16.	Nonequilibrium	"	0.25	"	1	"
17.	Frozen	"	"	"	"	"
18.	Nonequilibrium	"	"	"	0.5	"
19.	Frozen	"	"	"	"	"
20.	"	"	"	"	0.1	"
21.	"	"	0.1	"	1	"
22.	Frozen with non equilibrium flow in the pores	Lennard-Jones	1	0.981	-	0.7
23.	Same	Solid Spheres	"	"	-	"
24.	"	Lennard-Jones	"	"	-	"
25.	"	"	"	"	-	"
26.	"	"	"	"	-	"
27.	"	"	0.1	"	-	"
28.	"	"	"	"	-	0.8
29.	"	"	"	"	-	0.7
30.	Nonequilibrium with non-equilibrium flow in the pores	"	"	"	-	"

θ	$\overline{r}$,Å	T_e,°K	T_w,°K	Method of Measuring p_i^*	$-f \cdot 10$	$G\dfrac{g}{cm^2 \cdot sec} \cdot 10^3$	Δ^*,cm	Δ^{**},cm
0	0	6660.8	2927 13	Knudsen	0.435	0.989	-0.0107	0.0701
"	"	"	2924.97	"	0.425	0.967	0.0123	0.0629
"	"	"	3449.65	Langmuir	0.402	0.831	0.0283	0.0589
"	"	"	3452.33	"	0.410	0.847	–	–
"	"	"	3407.489	"	0.3757	0.6114	–	–
"	"	"	3407.543	"	0.3761	0.6116	0.0210	0.0434
"	"	"	3411.225	"	0.3865	0.628	0.0085	0.0477
"	"	"	3536.65	"	0.604	0.860	0.0309	0.0410
"	"	"	3370.5	"	0.303	0.464	–	–
"	"	9430	3554.1	"	0.723	1.40	–	–
"	"	"	3544.3	"	0.678	1.32	–	–
"	"	6660.8	3570.7	"	0.355	1.94	–	–
"	"	"	3574.0	"	0.363	1.97	–	–
"	"	"	3319.6	"	0.378	0.306	–	–
"	"	"	3323.3	"	0.388	0.324	–	–
"	"	"	3210.1	"	0.378	1.31	–	–
"	"	"	3213.7	"	0.390	1.35	–	–
"	"	"	3292.6	"	0.378	1.27	–	–
"	"	"	3295.9	"	0.388	1.31	–	–
"	"	"	3503.1	"	0.384	1.21	–	–
"	"	"	3267.4	"	0.390	2.09	–	–
0.4	10	660.8	2033.7	⌐	0.8148	2.063	–	–
"	"	"	1893.3	–	0.8152	1.85	–	–
"	20	"	2033.6	–	0.8154	2.064	–	–
0.5	10	"	2013.5	–	0.892	2.27	–	–
0.4	"	"	1892.4	–	0.780	2.00	–	–
0	0	"	2648.8	–	0.00105	0.00779	–	–
0.4	10	"	2598.6	–	0.351	2.65	–	–
"	"	"	2692.2	–	0.370	2.73	–	–
"	"	"	2762.1	–	0.350	2.21	–	–

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body with $R = 1m$. The state of the gas at the outer limit of the
layer was assumed to be equilibrium. In all the calculations we
calculated the transfer coefficients on the basis of the formulas
given in Section 5 of Chapter 1. Approximating polynomials were
used for the constants of equilibrium and enthalpies [20]. When
the calculation was performed using the Lennard-Jones model tables
of collision integrals from Hirshfelder et al [4] were fed into
the memory of the computer. The collision integrals in the tables
were tabulated in the form of a function of the corrected temper-
ature $T^* = kT/\varepsilon$ where ε/k is the parameter of the potential function
of the intermolecular reaction. For intermediate values of T^* /98
interpolations were automatically performed on the computer.

We may divide all the calculations into two groups. In calcu-
lations No. 1 - 21 the blackness coefficient was assumed to be
equal to zero. At surface temperatures of $\sim$ 3,000°K (as follows
from the evaluations in Chapter 3, Section 3, Subsection 3) we may
assume that the boundary conditions for a nonporous surface depend
only on the sublimation rate. Calculations for a porous surface
with $\varepsilon = 0$ were not made since experiments were performed by Eyring
and Blyholder only up to a surface temperature of $\sim$ 2,000°K and
extrapolations of the experimental results for substantially higher
temperatures of the coating may be incorrect. In all the calcula-
tions for this group we assumed that evaporation occurs only in
the form of C atoms.

Let us look at calculation No. 8 in which we took into account
the final rate of heterogeneous processes on the surface of a
graphite coating, [46]. In the gas phase the following components
were studied

$$C, \ CO, \ CO_2, \ O, \ O_2$$

and the reactions

1) $CO + O \rightleftharpoons CO_2$;	(3.3.I)
2) $3O \rightleftharpoons O + O_2$;	(3.3.II)
3) $O_2 + 2O \rightleftharpoons 2O_2$;	(3.3.III)
4) $C + O \rightleftharpoons CO$.	(3.3.IV)
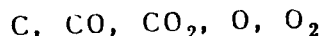
In the literature we did not find the recombination reaction rates
(3.3.I) and (3.3.IV) which occur via triple collisions. Therefore,
we applied a hypothesis of thermal expansion (see Chapter 2, Sec-
tion 1) to these reactions. Reaction rate constants (3.3.II) and
(3.3.III) are given in Table 4. Thus, the entire system of equa-
tions in this case is written in the form:

$$(l f_{\lambda\lambda})_\lambda + f f_{\lambda\lambda} + \frac{1}{2}\left(\frac{\rho_e}{\rho} - f_\lambda^2\right) = 0; \qquad (3.3.1)$$

$$\left(\frac{\gamma l}{\Pr}t_\lambda\right)_\lambda + t_\lambda\left(f\gamma - \frac{M_1}{R}\sum_{\alpha=1}^{5}c_{p\alpha}\bar{I}_{\alpha\lambda}M_\alpha\right) = \sum_{\alpha=1}^{5}H_\alpha M_\alpha[(\bar{I}_{\alpha\lambda})_\lambda - f\bar{c}_{\alpha\lambda}]; \qquad (3.3.2)$$

$$(\bar{I}_{1\lambda})_\lambda - f\bar{c}_{1\lambda} = \frac{1}{2u_{es}}k_{f4}\left[\bar{c}_2 - \bar{c}_1\bar{c}_4\Big/\bar{K}_{p4}\sum_{\alpha=1}^{5}\bar{c}_\alpha\right]; \qquad (3.3.3)$$

$$(\bar{I}_{2\lambda})_\lambda - f\bar{c}_{2\lambda} = -(\bar{I}_{3\lambda})_\lambda + f\bar{c}_{3\lambda}; \qquad (3.3.4) \qquad \underline{/99}$$

$$(\bar{I}_{3\lambda})_\lambda - f\bar{c}_{3\lambda} = \frac{1}{2u_{es}}\left\{-k_{f1}\left[\bar{c}_3 - \bar{c}_2\bar{c}_4\Big/\bar{K}_{p1}\sum_{\alpha=1}^{5}\bar{c}_\alpha\right]\right\}; \qquad (3.3.5)$$

$$(\bar{I}_{5\lambda})_\lambda - f\bar{c}_{5\lambda} = \frac{1}{2u_{es}}\left\{-k_{f3}\rho\left[\bar{c}_5^2 - \bar{c}_4^2\bar{c}_5\Big/\bar{K}_{p2}\sum_{\alpha=1}^{5}\bar{c}_\alpha\right] - \right.$$
$$\left. -k_{f2}\rho\left[\bar{c}_4\bar{c}_5 - \bar{c}_4^3\Big/\bar{K}_{p2}\sum_{\alpha=1}^{5}\bar{c}_\alpha\right]\right\}; \qquad (3.3.6)$$

$$\sum_{\alpha=1}^{5}\bar{c}_\alpha M_\alpha = 1. \qquad (3.3.7)$$

Here and below we use the symbol $\bar{K}_{pi} = k_{pi}/p_e$. As we already mentioned above with coating temperatures of $\sim 3,000°K$ the boundary conditions may be written without taking into account the heterogeneous reactions (3.2.II) - (3.2.IV), i.e., in the form:

$$\lambda = 0, \quad \bar{c}_1 = \frac{1}{M_1} + \bar{I}_{1\lambda}/f; \qquad (3.3.8)$$

$$\bar{c}_\alpha = \bar{I}_{\alpha\lambda}/f, \quad \alpha = 2, ..., 5; \qquad (3.3.9)$$

$$f\frac{L}{T_e R} + \frac{\gamma}{\Pr}t_\lambda = 0; \qquad (3.3.10)$$

$$f = -\frac{AM_1}{\sqrt{4\pi M_1 RT_w}\,\rho_w\eta_w u_{es}}\left[p_1^* - p_e\left(\bar{c}_{1w}\Big/\sum_{\alpha=1}^{5}\bar{c}_\alpha\right)\right]; \qquad (3.3.11)$$

$$f_\lambda = 0 \qquad (3.3.12)$$

$$\lambda = \infty, \quad t = 1, \quad f_\lambda = 1, \quad \bar{c}_\alpha = \bar{c}_{\alpha e}. \qquad (3.3.13)$$

Thus, the concentration c_{1w} is depleted in the calculation process and we can explain the evaporation mechanism.

In the other calculations of the first group (i.e., Nos. 1-7 and Nos. 10-21, Table 5) the surface is assumed to be catalytic. For the case of a catalytic wall (as follows from the preliminary estimations and results of the work by Shchennikov [25]) for wall temperatures of $\sim 3,000°K$ concentrations of C and C_2 everywhere, including the surface of the body, are negligible ($\sim 10^{-6}$) and we may assume the evaporation to be kinetic. In accordance with this the Hertz-Knudsen equation is written:

$$(\rho v)_1 = A M p_1^* / \sqrt{2\pi M_1 R T_w} \ . \tag{3.3.14}$$

Thus, in these calculations the following system of reactions in
the gas phase was studied:

$$
\begin{array}{lll}
1) & CO_2 \rightleftharpoons CO + O; & (3.3.\text{V}) \\
2) & O + O_2 \rightleftharpoons 3O; & (3.3.\text{VI}) \\
3) & 2O_2 \rightleftharpoons 2O + O_2 \ . & (3.3.\text{VII})
\end{array}
$$

The boundary conditions (3.3.8) and (3.3.9) were replaced by the
equations of equilibrium and conservation of the element (0):

$$
\left.
\begin{aligned}
&\sum_{\alpha=1}^{5} \bar{c}_\alpha M_\alpha = 1, \quad \bar{c}_5 = \bar{c}_4^2 \Big/ \sum_{\alpha=2}^{5} \bar{c}_\alpha \bar{K}_{p2} , \quad \bar{c}_3 = \bar{c}_2 \bar{c}_4 \Big/ \sum_{\alpha=2}^{5} \bar{c}_\alpha \bar{K}_{p1} ; \\
&\bar{I}_{2\lambda} - f \bar{c}_2 + \bar{I}_{4\lambda} - f \bar{c}_4 + 2(\bar{I}_{3\lambda} - f \bar{c}_3 + \bar{I}_{5\lambda} - f \bar{c}_5) = 0 .
\end{aligned}
\right\} \tag{3.3.15}
$$

In the gas phase equations (3.3.3) - (3.3.6) were replaced for the
frozen boundary layer by the equation

$$(\bar{I}_{2\lambda})_\lambda - f \bar{c}_{\alpha\lambda} = 0, \quad \alpha = 2, \dots, 5. \tag{3.3.16}$$

For an equilibrium boundary layer, as we know, μ equations of con-
tinuity are replaced by $\mu - \nu$ equations of equilibrium and ν equa-
tions of discontinuity for elements. In order to apply the numer-
ical method described below it was convenient after taking the
logarithm of the equations of equilibrium twice to differentiate
them over λ reducing the equations of equilibrium to a differential
equation of the second order of the type

$$
\bar{c}_3'' \frac{\bar{c}_2 \bar{c}_4}{\sum\limits_{\alpha=2}^{5} \bar{c}_\alpha} + \bar{c}_3' \left(\frac{\bar{c}_2 \bar{c}_4}{\sum\limits_{\alpha=2}^{5} \bar{c}_\alpha} f_{2T}' T_e t_\lambda \right) +
$$

$$
+ \bar{c}_3 \left[\left(\frac{\bar{c}_2 \bar{c}_4}{\sum\limits_{\alpha=2}^{5} \bar{c}_\alpha} f_{2T}' T_e t_\lambda \right)' - \left(\frac{\bar{c}_2 \bar{c}_4}{\sum\limits_{\alpha=2}^{5} \bar{c}_\alpha} \right)'' \right] = 0 ; \tag{3.3.17}
$$

$$
\bar{c}_5'' \frac{\bar{c}_4^2}{\sum\limits_{\alpha=2}^{5} \bar{c}_\alpha} + \bar{c}_5' \left(\frac{\bar{c}_4^2}{\sum\limits_{\alpha=2}^{5} \bar{c}_\alpha} f_{1T}' T_e t_\lambda \right) +
$$

$$
+ \bar{c}_5 \left[\left(\frac{\bar{c}_4^2}{\sum\limits_{\alpha=2}^{5} \bar{c}_\alpha} f_{1T}' T_e t_\lambda \right)' - \left(\frac{\bar{c}_4^2}{\sum\limits_{\alpha=2}^{5} \bar{c}_\alpha} \right)'' \right] = 0 , \tag{3.3.18}
$$

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where $f_1(T)$ and $f_2(T)$ are certain functions which pertain to poly- nomials that approximate the equilibrium constants $\overline{K}_{p1}$ and $\overline{K}_{p2}$: Calculation No. 9 was made for a case of the streamline flow of graphite by air and includes the components CO, CO_2, O, O_2, N, N_2 and NO.

The reactions studied:

$$CO_2 \rightleftharpoons CO + O; \qquad (3.3.VIII)$$
$$O_2 \rightleftharpoons 2O; \qquad (3.3.IX)$$
$$N_2 \rightleftharpoons 2N; \qquad (3.3.X)$$
$$NO \rightleftharpoons N + O. \qquad (3.3.XI)$$

We assumed the wall to be catalytic. Conditions at the outer limit of the boundary layer:

$$f_\lambda = 1, \quad t = 1, \quad \overline{c}_2 = 0, \quad \overline{c}_3 = 0, \quad \overline{c}_4 = 0.1503 \cdot 10^{-1}, \quad \overline{c}_5 = 0,$$
$$\overline{c}_6 = 0.1911 \cdot 10^{-1}; \quad \overline{c}_7 = 0.1733 \cdot 10^{-1}; \quad \overline{c}_8 = 0.2165 \cdot 10^{-3}.$$

In concluding the survey of calculations of the first group let us note that in calculations No. 1 and 2 we assumed that the pressure of the saturated carbon vapor corresponds to results of an experiment performed on the basis of the Knudsen method, and in the other calculations, on the basis of the Langmuir method (see Chapter 2, Section 3).

In calculations of the second group (Nos. 22 - 30) the coefficient of blackness of the surface was assumed to be 0.7 (except in calculation No. 28 where $\varepsilon = 0.8$). We were able to disregard the sublimation of the body since the surface temperature was sufficiently low (see Chapter 3, Section 3, Subsection 3). Thus, in the gas phase and in the pores of the body four components were taken into account: O, O_2, CO and CO_2. In the gas phase the following reactions were studied:

$$1) \quad 2O_2 \rightleftharpoons 2O + O_2; \qquad (3.3.XII)$$
$$2) \quad O + O_2 \rightleftharpoons 3O; \qquad (3.3.XIII)$$
$$3) \quad CO_2 \rightleftharpoons CO + O; \qquad (3.3.XIV)$$
$$4) \quad CO + O_2 \rightleftharpoons CO_2 + O. \qquad (3.3.XV)$$

In the pores of the body and on the surface

$$5) \quad C_{graphite} + O \longrightarrow CO; \qquad (3.3.XVI)$$
$$6) \quad C_{graphite} + \tfrac{1}{2}O_2 \longrightarrow CO; \qquad (3.3.XVII)$$
$$7) \quad C_{graphite} + CO_2 \longrightarrow 2CO. \qquad (3.3.XVIII)$$

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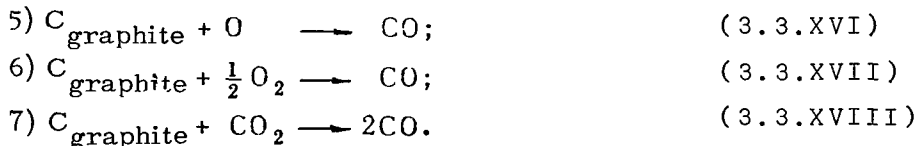
Let us give the complete system of equations and boundary conditions for calculation No. 30 in which the final reaction rates in the gas phase and in the pores of the body are taken into account [47].

The gas phase:

$$(l f_{\lambda\lambda})_\lambda + f f_{\lambda\lambda} + \frac{1}{2}\left(\frac{\rho_e}{\rho} - f_\lambda^2\right) = 0; \tag{3.3.19}$$

$$\left(\frac{\gamma l}{\Pr} t_\lambda\right)_\lambda + t_\lambda\left(f\gamma - \frac{M_1}{R}\sum_{\alpha=2}^{5} c_{p\alpha}\overline{I}_{\alpha\lambda}M_\alpha\right) = \sum_{\alpha=2}^{5} H_\alpha M_\alpha[(\overline{I}_{\alpha\lambda})_\lambda - f\overline{c}_{\alpha\lambda}]; \tag{3.3.20}$$

$$(\overline{I}_{2\lambda})_\lambda - f\overline{c}_{2\lambda} + (\overline{I}_{3\lambda})_\lambda - f\overline{c}_{3\lambda} = 0; \tag{3.3.21}$$

$$(\overline{I}_{3\lambda})_\lambda - f\overline{c}_{3\lambda} = \frac{1}{2u_{es}}\left[-k_{f3}\left(\overline{c}_3 - \overline{c}_2\overline{c}_4\Big/\overline{K}_{p3}\sum_{\alpha=2}^{5}\overline{c}_\alpha\right) + \right.$$
$$\left. + k_{f4}\rho(\overline{c}_2\overline{c}_5 - \overline{c}_3\overline{c}_4/k_{p4})\right]; \tag{3.3.22}$$

$$\sum_{\alpha=2}^{5}\overline{c}_\alpha M_\alpha = 1; \tag{3.3.23}$$

$$(\overline{I}_{5\lambda})_\lambda - f\overline{c}_{5\lambda} = -\frac{\rho}{2u_{es}}\left[\left(\overline{c}_5 - \overline{c}_4^2\Big/\sum_{\alpha=2}^{5}\overline{c}_\alpha\overline{K}_{p1}\right)(\overline{c}_5 k_{f1} + \overline{c}_4 k_{f2}) + \right.$$
$$\left. + k_{f3}(\overline{c}_2\overline{c}_5 - \overline{c}_3\overline{c}_4/k_{p4})\right], \tag{3.3.24}$$

where (3.3.21) is the equation of continuity for the element C. Equations of diffusion for the pores of the material (see Note 3, Chapter 2, Section 5):

$$\overline{r} D_2 n_2'' = -2(1-\theta)\Phi\,\frac{2n_3 + n_4 + 2n_5}{n_3 + n_4 + 2n_5}; \tag{3.3.25}$$

$$\overline{r} D_\alpha n_\alpha'' = 2(1-\theta)\Phi\,\frac{n_\alpha}{n_3 + n_4 + 2n_5}, \qquad \alpha = 3,4,5. \tag{3.3.26}$$

Boundary conditions:

$$\lambda = +\infty: \quad t = 1,\; f_\lambda = 1,\; \overline{c}_2 = \overline{c}_3 = 0,\; \overline{c}_4 = \overline{c}_{4e},\; \overline{c}_5 = \overline{c}_{5e}; \tag{3.3.27}$$

$$\lambda = 0: \quad \frac{\gamma}{\Pr}t_\lambda\frac{T_e R\sqrt{2\rho_w\eta_w u_{es}}}{M_1} - \overline{U}_3 Q_7 - \overline{U}_4 Q_5 - \overline{U}_5 Q_6 = \varepsilon\sigma T_w^4; \tag{3.3.28}$$

$$\overline{c}_\alpha f = \overline{I}_{\alpha\lambda} - \overline{U}_\alpha\Big/\sqrt{2\rho_w\eta_w u_{es}}, \quad \alpha = 2,\dots,5; \tag{3.3.29}$$

$$f = -\sum_{\alpha=2}^{5}\overline{U}_\alpha\Big/\sqrt{2\rho_w\eta_w u_{es}}, \quad f_\lambda = 0; \tag{3.3.30}$$

$$y = +\infty: \; n_\alpha' = 0, \quad \alpha = 2,\dots,5, \tag{3.3.31}$$

where $U_\alpha = \pi r^2 n_p m_\alpha D_\alpha n_\alpha'$, $\alpha = 2, \ldots, 5$ and ϕ is determined by (2.4.14):

$$\Phi = 1.55 \cdot 10^{11} T_w^{3/4} \sqrt{k} \, e^{-E/R \, T_w} \sqrt{n_4 + 2n_5 + n_3}.$$

Calculations Nos. 22-29 pertain to the frozen boundary layer. However, the flow in the pores was assumed to be nonequilibrium as before. In accordance with this conditions in (3.4.29) were replaced by the following boundary conditions:

$$\bar{c}_2 \bar{c}_5 = \frac{\bar{c}_3 \bar{c}_4}{k_{p4}}; \quad \bar{c}_5 = \bar{c}_4^2 \Big/ \sum_{\alpha=2}^{5} \bar{c}_\alpha \bar{K}_{p1}; \quad \sum_{\alpha=2}^{5} \bar{c}_\alpha M_\alpha = 1; \qquad (3.3.32)$$

$$\bar{I}_{4\lambda} - f\bar{c}_4 + \bar{I}_{2\lambda} - f\bar{c}_2 + 2[\bar{I}_{5\lambda} - f\bar{c}_5 + \bar{I}_{3\lambda} - f\bar{c}_3] = 0. \qquad (3.3.33)$$

Equation (3.3.33) is an equation of continuity for element 0. Writing the equations of a frozen boundary layer in a gas phase is done in the usual way (Chapter 3, Section 2) and we will not do it here.

Concluding the investigation of calculations Nos. 22 - 30, let us note that calculation No. 26 in contrast to the others is performed without taking into account the Eucken correction (see Chapter 1, Section 4, Subsection 3) for the internal degrees of freedom of monatomic molecules.

Note. As follows from what we have said above in formulating the boundary conditions for a frozen boundary layer in order to complete the task we had to make several assumptions with respect to the chemical properties of the surface. We assumed that detailed equilibrium exists on the surface. In fact, even in equilibrium boundary layer theory on a sublimating surface the assumption is not clearly made that one of the heterogeneous reactions occurs in a substantially nonequilibrium way, i.e., the reaction $C_{graphite} \rightleftarrows C_{gas}$ for whose rate the Hertz-Knudsen equation was written.

Assuming an equilibrium flow of chemical reactions on the surface of a body is not the only means of completing the task in frozen boundary layer theory. In fact, let us look at another possibility of completing frozen boundary layer equations using the specific kinetics of heterogeneous reactions on the surface of graphite obtained in experiments by Eyring and Blyholder [31, 32].

For calculations of the first group ($\varepsilon = 0$) which were made for a nonporous surface a predominant effect of the sublimation reaction was established. But in the absence of reactions in the gas phase this means that the problem leads to the solution of boundary layer equations for a binary gas mixture of 0, C (the con-

centration of O_2 at the outer limit of the layer is negligibly small). The boundary conditions of the problem:

$$\frac{\gamma}{Pr} t_\lambda + f \frac{L}{T_e R} = 0; \quad f_\lambda = 0; \quad M_1 \bar{c}_1 + M_4 \bar{c}_4 = 1; \tag{3.3.34}$$

$$\bar{I}_{4\lambda} - f \bar{c}_4 = 0, \quad f = -A M_1 \left(p_1^* - p_e \frac{\bar{c}_{1w}}{\bar{c}_{1w} + \bar{c}_{4w}} \right) \Big/ \sqrt{4\pi M_1 R u_{es} \rho_w \eta_w T_w}, \tag{3.3.35}$$

here L is the sublimation energy ($\sim$ 171 kCal/mole). The boundary conditions at the outer limit of the boundary layer are written in the usual way.

In calculations of the second group ($\varepsilon \neq 0$), which were made for a porous surface, we could also look at only two components, i.e., 0, CO, since sublimation at temperatures of $\sim 2000°K$, as we have explained, is negligible in comparison with the effect of heterogeneous combustion reactions on parameters of the boundary layer. Thus, the boundary conditions of the problem:

$$\frac{\gamma}{Pr} t_\lambda - \frac{fQ}{T_e R} = \frac{M_1 \varepsilon \sigma T_w^4}{T_e R \sqrt{2\rho_w \eta_w u_{es}}}; \tag{3.3.36}$$

$$M_2 \bar{c}_2 + M_4 \bar{c}_4 = 1; \quad \bar{I}_{2\lambda} - f \bar{c}_2 + \bar{I}_{4\lambda} - f \bar{c}_4 = 0; \tag{3.3.37}$$

$$f = -\pi \bar{r}^2 n_p m_1 (1-\theta) \int_0^\infty \Phi \, dy \Big/ \sqrt{2\rho_w \eta_w u_{es}}, \tag{3.3.38}$$

where Q is the heat of the reaction $C_{graphite} + 0 \rightarrow CO$. It is understood that prior to performing the experiments or calculating the chemically nonequilibrium boundary layer there is no reason to give preference to one formulation of the problem. In our calculations the degree of accuracy of the above formulation of the frozen boundary layer with a detailed chemical equilibrium on the outer surface of the graphite was controlled by calculations of the chemically nonequilibrium boundary layer taking into account the final rate of heterogeneous reactions. For calculations of the first group this is calculation No. 8 and for calculations of the second group it is calculation No. 30.

However, we must note that integration of frozen boundary /105 layer equations can be done much more easily on electronic computers than nonequilibrium boundary layer equations. Moreover, frozen boundary layer equations permit analytical methods of investigation. Therefore, it is advisable to perform engineering calculations using frozen boundary layer conditions and controlling calculations in a random way by means of experiments or calculations

of the chemically nonequilibrium boundary layer.

For certain types of problems (for example, the interaction of a shock wave with the boundary layer) the values for the displacement thickness (Δ^*) and the pulse loss (Δ^{**}) are of interest. As we know,

$$\Delta^* = \int_0^\infty \left(1 - \frac{\rho}{\rho_e}\frac{u}{u_e}\right) dy; \tag{3.3.39}$$

$$\Delta^{**} = \int_0^\infty \frac{\rho u}{\rho_e u_e}\left(1 - \frac{u}{u_e}\right) dy. \tag{3.3.40}$$

In Dorodnitsyn variables:

$$\Delta^* = \int_0^\infty \left(1 - f_\lambda \frac{\sum_\alpha \bar{c}_{\alpha e}}{\sum_\alpha \bar{c}_\alpha t}\right)\frac{\sqrt{2\xi}}{r u_e \rho}\, d\lambda; \tag{3.3.41}$$

$$\Delta^{**} = \int_0^\infty \frac{\sum_\alpha \bar{c}_{\alpha e}}{\sum_\alpha \bar{c}_\alpha t} f_\lambda(1-f_\lambda)\frac{\sqrt{2\xi}}{r u_e \rho}\, d\lambda, \tag{3.3.42}$$

at the critical point:

$$\Delta^* = \sqrt{\frac{\rho_w \eta_w}{2 u_{es}}}\frac{1}{\rho_e}\left[\int_0^\infty (1-f_\lambda) d\lambda - \int_0^\infty \left(1 - t\frac{\sum_\alpha \bar{c}_\alpha}{\sum_\alpha \bar{c}_{\alpha e}}\right) d\lambda\right]; \tag{3.3.43}$$

$$\Delta^{**} = \sqrt{\frac{\rho_w \eta_w}{2 u_{es}}}\frac{1}{\rho_e}\int_0^\infty (1 - f_\lambda) f_\lambda\, d\lambda. \tag{3.3.44}$$

The values of these magnitudes (in cm) for some of the calculations are given in Table 5. Let us note that in calculation No. 1 a negative displacement thickness was obtained. This is because the density ρ_w on the surface of the coating is substantially more than the density at the outer limit of the boundary layer ρ_e. The value $\rho_w > \rho_e$ by virtue of the fact that $T_w < T_e$ and the mean molecular weight of the mixture on the surface $1/\sum_\alpha \bar{c}_{\alpha w} > 1/\sum_\alpha \bar{c}_{\alpha e}$ as a result of the predominance of heavy components on the surface (Fig. 20).

In Figure 21 we have represented the functions $c_\alpha(\lambda)$, $f(\lambda)$ and $t(\lambda)$ for calculations Nos. 3 and 4 (the curves representing the frozen boundary layer are drawn by dashes).

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In Figure 22 we show the functions $c_\alpha(\lambda)$, $f(\lambda)$ and $t(\lambda)$ for an equilibrium (continuous), frozen (dashed lines) and non-equilibrium boundary layer with a catalytic wall (dash-dotted lines), i.e., the results of calculations Nos. 5, 6, and 7.

In Figure 23 analogous functions are drawn for calculation No. 8 which was made for a nonequilibrium boundary layer taking into account the final velocity of heterogeneous reactions, and for calculation No. 6. of a nonequilibrium boundary layer with a catalytic wall (dashed lines).

In Figure 24 we have given the results of calculating the streamline flow of graphite by air (calculation No. 9).

In Figure 25 we give the results of calculating the chemically nonequilibrium boundary layer (No. 30) taking into account the final rate of heterogeneous reactions and the frozen layer with a catalytic outer surface and a nonequilibrium flow in the pores of the body (dashed line).

Figure 26 shows the distribution of concentrations in the pores of the graphite for these calculations (here and below $\bar{n}_\alpha = n_\alpha/n_{5w}$.

In Figure 27 for the same calculations (Nos. 29 and 30) the distributions $Pr(\lambda)$, $\kappa(\lambda)$ and $\eta(\lambda)$ are drawn for a nonequilibrium boundary layer and the frozen layer (dashed lines). As we see from Figure 27 the Pr number during the change across the boundary layer fluctuates smoothly around the value 0.7 and differs little from it.

In Figure 28 $c_\alpha(\lambda)$, $f(\lambda)$ and $t(\lambda)$ represent calculations No. 22 (solid lines) and No. 25 (dashed lines). Let us note that the values of the functions $c_\alpha(\lambda)$, $f(\lambda)$ and $t(\lambda)$ for calculation No. 24 in which the radius of the pores is assumed to be 20 Å practically coincides with their values in calculation No. 22 ($\bar{r}$ - 10 Å).

In Figure 29 the distributions $n_\alpha(y)$ represent the calculations No. 22 (solid lines), No. 25 (dashed lines) and No. 24 (dash-dotted lines). Thus, in Figure 28 and 29 the values which characterize the boundary layer for graphite are compared with the different radius of the pores and the porosity.

In Figure 30 the distributions $Pr(\lambda)$ and $\kappa(\lambda)$ are given for calculations No. 22 (solid lines) and No. 26 (dashed lines), and thereby the effect of the Eucken correction on the distribution of the Pr number and the thermal conductivity of the gas mixture across the boundary layer is explained.

Figures 31 and 32 permit judging the nature of the approach to detailed equilibrium. As an example graphs of the functions

$$\phi_1 = \bar{c}_5 - \bar{c}_4^2 / \sum_{\alpha=2}^{5} \bar{c}_\alpha \bar{K}_{p2} \quad \text{(Fig. 31) and} \quad \phi_2 = 2\rho u_{es} [(\bar{I}_{5\lambda}) - \bar{f} c_{5\lambda}] \text{ are}$$
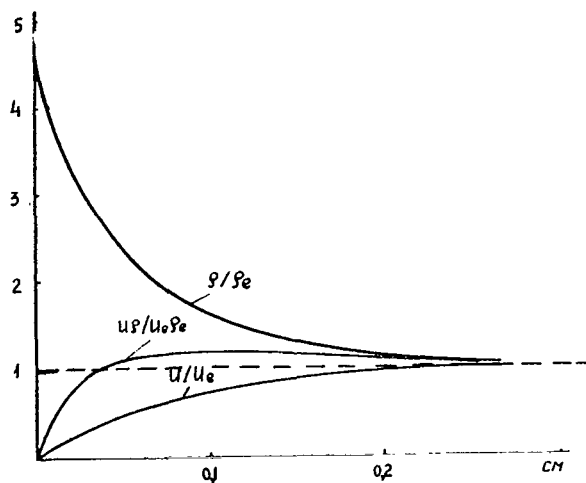
Fig. 20

Fig. 21

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Fig. 22
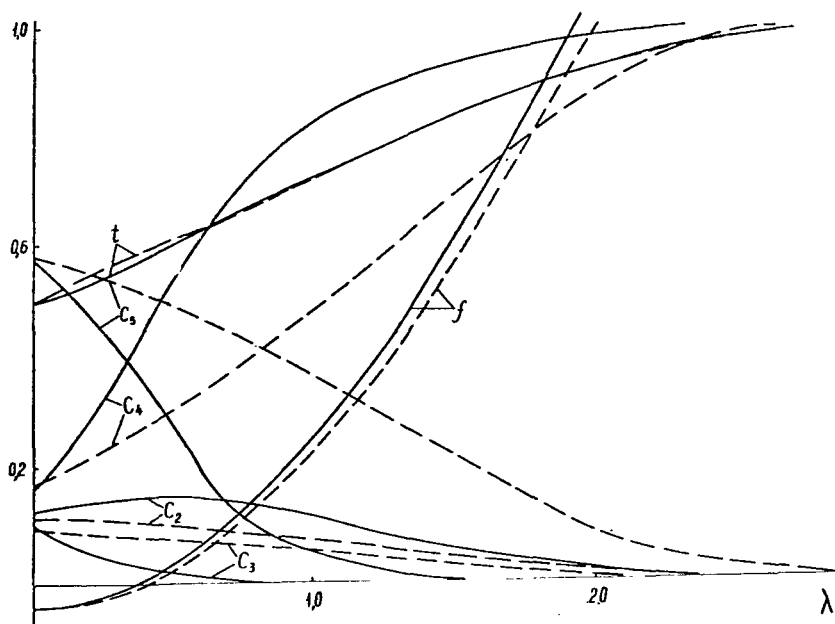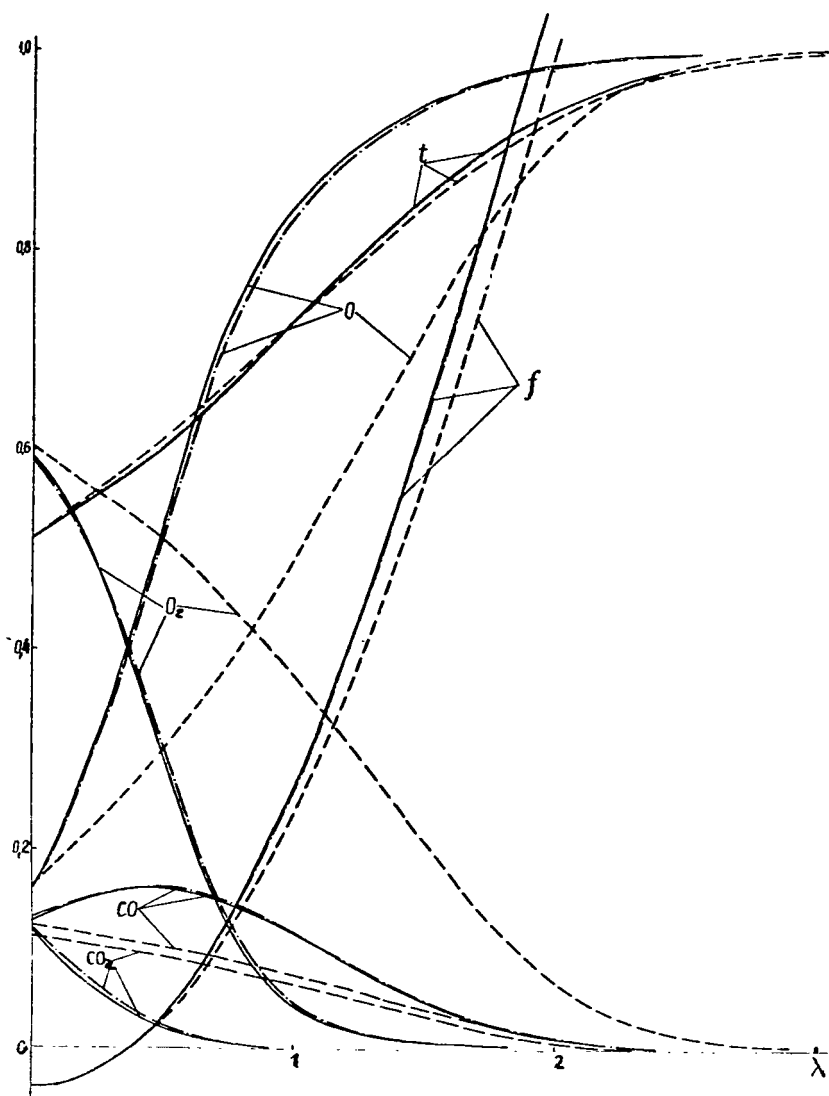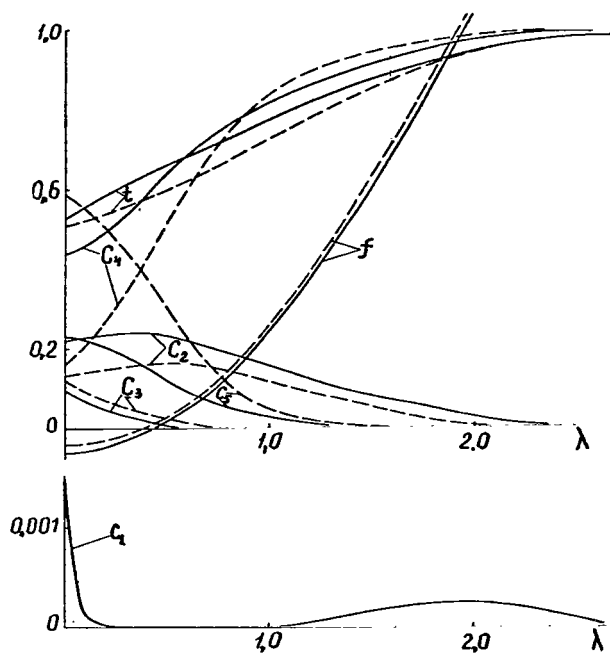
Fig. 23

Fig. 24

98
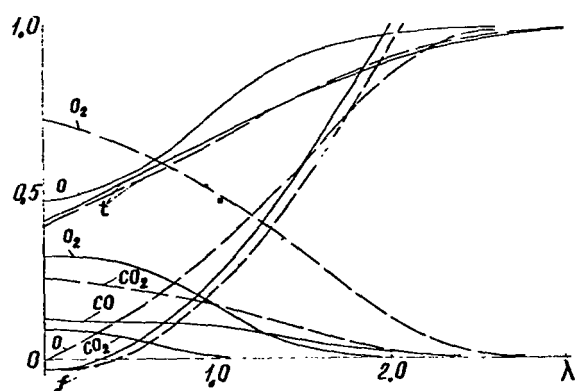
Fig.   25

Fig. 26

Fig. 27
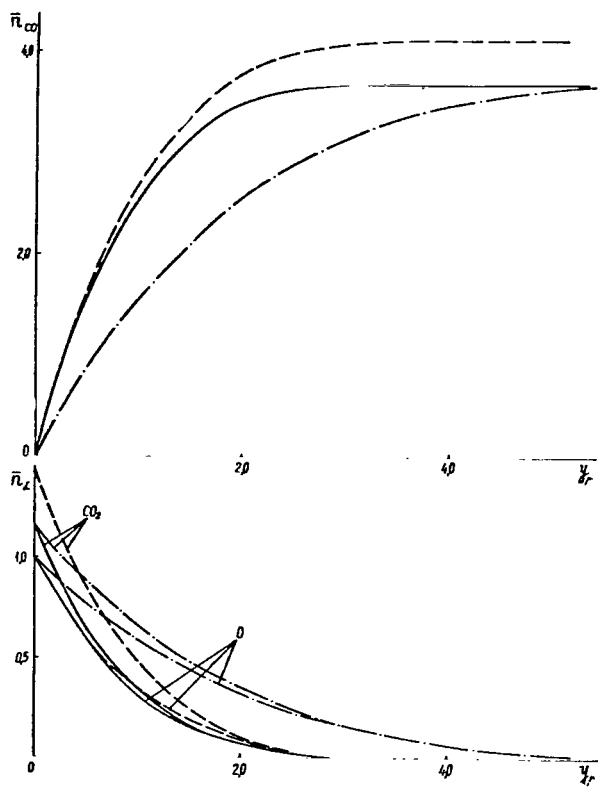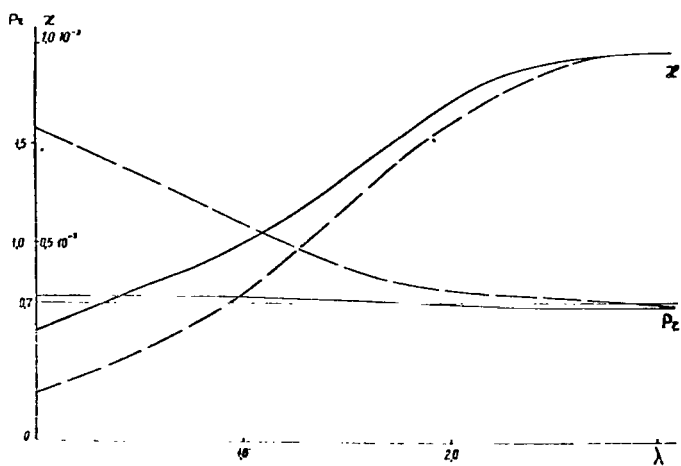
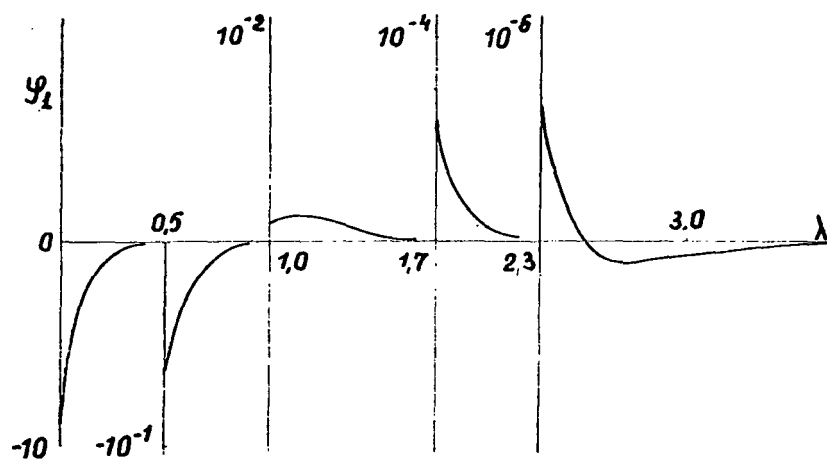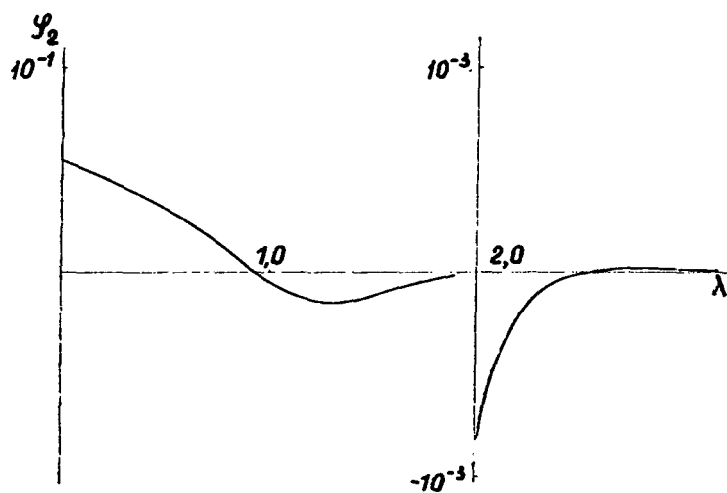Fig. 28

100
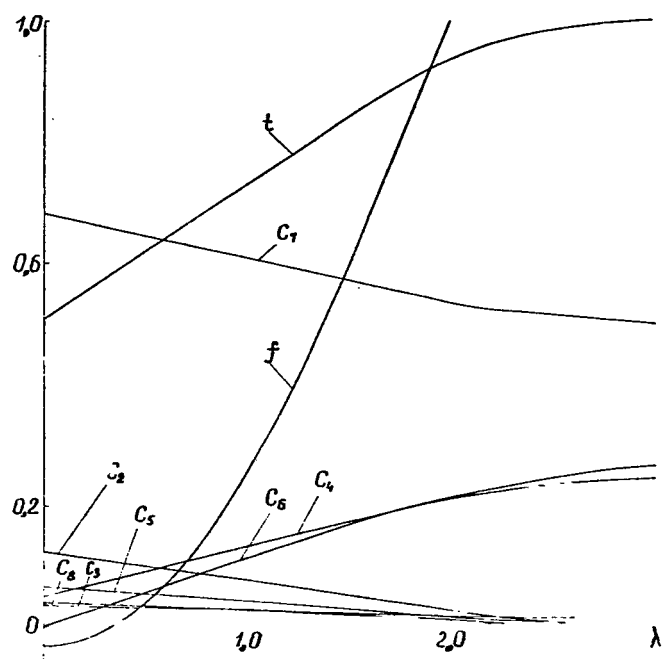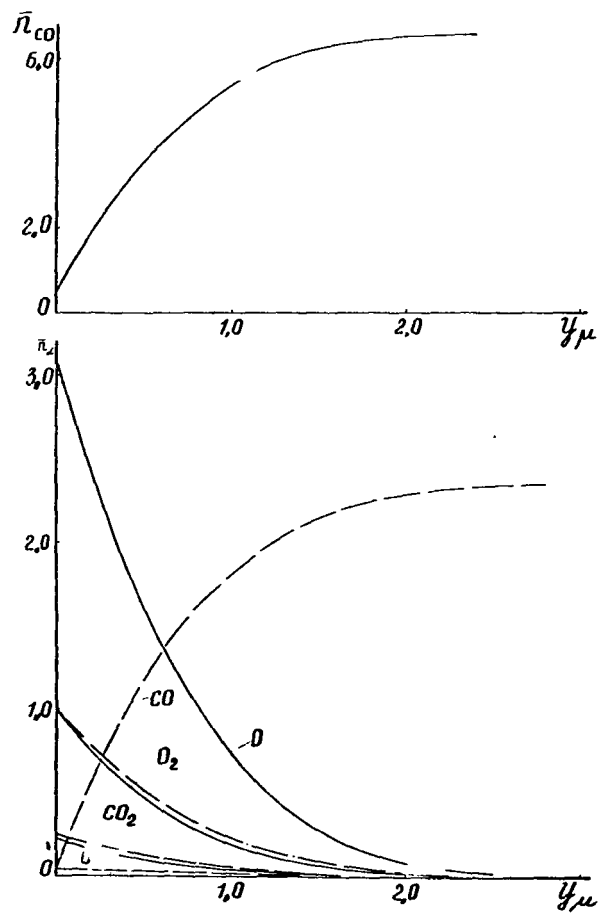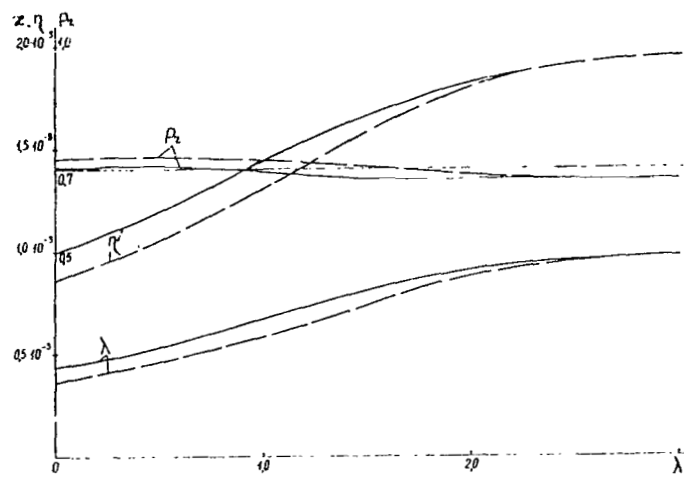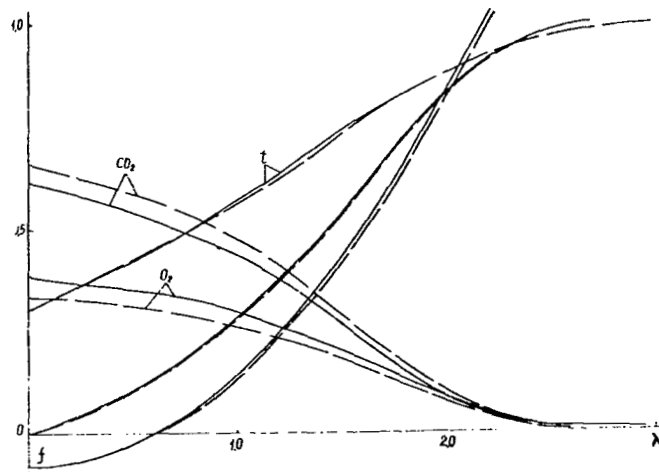
Fig. 29

Fig. 30

Fig. 31

Fig. 32

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represented in a discontinuous scale (Fig. 32). As we can easily see, function ϕ_2 characterizes the convective and diffusion transfer of the O_2-component across the boundary layer.

4. Method and some Results of Numerical Calculations in the Vicinity of the Critical Point

Systems of equations given in Section 4 were solved numerically on the electronic computer on the basis of the method of successive approximations. The order of solution was the following. A linear profile for the concentrations $\bar{c}_\alpha(\lambda)$, and temperature $t(\lambda)$ and in the form of quadratic parabolas for $f(\lambda)$ and $\bar{\pi}_\alpha(\lambda)$ was given as first approximation. Then using the method described in [48] the pertinent systems of equations were solved. After this, the following approximation for t_w, $\bar{c}_{\alpha w}$ and f_w was found by means of the boundary conditions, and in calculations of the first group ($\varepsilon = 0$) the surface temperature was determined from the Hertz-Knudsen equation and f_w from the energy balance equation on the surface. The integration step was constant and changed in the range of 0.05-0.1, except for calculation No. 8. The program for calculating the chemically nonequilibrium boundary layer was arranged in such a way as to operate with any group of steps. This was done so as to eliminate any effect from the value of the step on the accuracy of calculating close to the wall where $\bar{c}_1(\lambda)$ undergoes a very sharp change. The described decision procedure resulted in the build-up of the solution and in the automatic shutdown of the computer even with the installation of buffers for the boundary conditions. The installation of buffers at all points was a way out of this situation. For the $(n + 1)$th iteration it was not the results of the n-th iteration of $f, \phi_i^{(n)}$ that served as the initial numerical material but rather $\phi_i^{(n)'}$, which with $\phi_i^{(n)}$ were connected by the relationship

$$\varphi_i^{(n)'} = \varphi_i^{(n-1)'} + \delta(\varphi_i^{(n)} - \varphi_i^{(n-1)'}). \qquad (3.4.1)$$

The size of the buffer δ was selected on the computer experimentally and changed in a range from 0.04 (equilibrium boundary layer) to 1 (several calculations of the frozen boundary layer). To find the solution, about 100 iterations were required.

From Table 5 and Figures 20-32 we can make the following conclusions, at least for the conditions studied at the outer boundary and for the shape of the body:

1. The values for T_w and G which were obtained by using conditions of a frozen, equilibrium and nonequilibrium boundary layer and a catalytic wall are almost the same. Generally, using a frozen layer model leads to a small increase in the temperature of the wall (in the range of $\sim 10°$ for the examples studied) and to the carrying away of the mass (in the range of 6%). Thus, if the model

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of the catalytic wall represents the physics of the process the use
of frozen boundary layer equations yields a completely satisfactory
accuracy for the values which are of greatest interest to practical
workers (G, T_w and $\bar{c}_{\alpha w}$). The concentration distribution for a
frozen layer and for the layer taking into account the chemical re-
actions in the gas phase differ much more. The concentrations of
components may differ by several times (see, for example, Fig. 25).
This leads to a substantial difference in the values Δ^*, Δ^{**}.

2. As we have already mentioned above (see Chapter 2, Section
3) the pressure p^* of saturated carbon vapors measured on the basis
of the Knudsen method is approximately 100 times more than p^* meas-
ured on the basis of the Langmuir method. However, calculations
using experimental data on the basis of the Knudsen method yielded
a surface temperature approximately 520° lower than T_w obtained in
"Langmuir" calculations. The carrying away of the mass of graphite
calculated on the basis of the Knudsen-Langmuir formula is propor-
tional to the pressure p^* which, in turn, depends exponentially on
the temperature. The substantial decrease in surface temperature
in the "Knudsen" calculations caused the carrying away of graphite
mass to be only 14% more than G (after Langmuir) (cf. calculations
Nos. 1-4).

3. Using the molecular reaction model of Lennard-Jones leads
(in comparison to the solid sphere model) to a certain increase in
surface temperature (~ 40°) and to a substantial increase in the
carrying away of the mass (up to 35%) (calculations Nos. 3 and 6
or Nos. 22 and 23).

4. Calculating the seven-component air (No. 9) showed a sig-
nificant decrease in the carrying away of the mass (~ 26%) on the
basis of a comparison with analogous calculations for the case of   /116
streamline flow of graphite with oxygen.

5. As we have already shown at surface temperatures of   ~3000°K
the carrying away of the mass, the temperature and the concentration
distribution on the wall are determined by sublimation of the body.
Thus, we may assume that calculation No. 8 pertains to the case of
a "chemically inert wall". During calculations the concentrations
$\bar{c}_{1w}$ which determined the sublimation process was worked out. The
pressure of saturated vapors for the surface temperature of this
calculation was $p_1^* = 0.00610$ atm and $p_1 = 0.00268$ atm. Thus the
evaporation process was in the intermediate region between the
kinetic and the diffusion evaporation. The calculation shows an
increase in temperature in comparison with the hypothetical cataly-
tic surface by approximately 130° and a substantial increase in the
carrying away of the mass. This is because of (see Fig. 23) the
rapid transfer of the evaporating carbon to the composition of other
compounds in a narrow zone close to the surface of the material. It
is also because of the increase in heat transfer to the material
and, consequently, the increase in carrying away of the mass (such
a substantial increase in the carrying away of the mass is due to

the exponential dependence of p^* on temperature). In addition, the difference in concentrations of the components on the wall is very great (for example, the concentration of O_2 in No. 8 was approximately 2.5 times more than for the case of a catalytic surface.)

6. Let us note that the tenfold decrease in the melting coefficient (from 1 to 0.1) leads to a substantial increase in surface temperature (approximately by 300°) and to some increase in the carrying away of the mass (~11%) (see calcualtions Nos. 16-20).

7. There is a very great discrepancy in the concentration distribution c_α for the frozen and nonequilibrium boundary layer taking into account the final rate of heterogeneous reactions in the pores of the graphite (see Fig. 25). The carrying away of the mass for the nonequilibrium boundary layer is approximately 19% lower and the temperature is approximately 70° higher than for the case of the frozen boundary layer.

8. The carrying away of the mass for the nonporous surface is 0.003 of the carrying away of the mass for the porous surface.

9. The carrying away of the mass and the temperature of the porous surface in practice do not depend on the radius of the pores for the heterogeneous kinetics of reaction which we have studied. However, the distribution of concentrations in the pores is very substantially different (see Fig. 29). For pores with r = 20 Å the yield for equilibrium distribution of concentrations occurs much more slowly than for a surface with r = 10 Å.

10. The calculation of polyatomic gas mixtures without the Eucken correction for the internal degress of freedom of polyatomic molecules leads to greatly increased values of the Pr number (see Fig. 30).

11. Let us note that for a porous graphite sphere ε = 0.7 and R = 1m the carrying away of the mass at the critical point was approximately twice that for a nonporous sphere ε = 0. However, with a decrease in the radius of the sphere the loss of mass as a result of sublimation grows substantially faster than as a result of combustion reactions (cf. calculations Nos. 21 and 29).

12. The approach to detailed equilibrium in the calculations of a nonequilibrium boundary layer was of a transient and varying nature; the state of the gas on the surface of the material was very far from detailed equilibrium. Let us note that the mass transfer as a result of convection and diffusion across the layer was also transient and varying (see Figs. 31 and 32).

5. Calculation of the Boundary Layer with Chemical Reactions along the Generatrix of the Body of Rotation.

Let us give the calculation of a chemically nonequilibrium layer along the generatrix of a graphite sphere. We assume that

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the rate of the heterogeneous reactions on the surface and in the pores of the material is finite. We compare the solution obtained with the calculation on the basis of the local similarity method and with the calculation of the frozen boundary layer.

The flow of the μ-component chemically nonequilibrium gas in the boundary layer is described by the following system of equations (see Chapter 1, Section 3):

$$(lf_{\lambda\lambda})_\lambda + ff_{\lambda\lambda} + 2\left(\frac{\rho_e}{\rho} - f_\lambda^2\right)\frac{d\ln u_e}{d\ln\xi} = 2\xi[f_\lambda f_{\lambda\xi} - f_\xi f_{\lambda\lambda}]; \qquad (3.5.1)$$

$$\left(\frac{\gamma l}{Pr}t_\lambda\right)_\lambda + t_\lambda\left[f\gamma - \frac{M_k}{R}\sum_{\alpha=1}^{\mu}c_{p\alpha}\overline{I}_{\lambda\lambda}M_\alpha\right] - \sum_{\alpha=1}^{\mu}H_\alpha M_\alpha[(\overline{I}_{\alpha\lambda})_\lambda -$$

$$-f\overline{c}_{\alpha\lambda}] + u_e^2 f_{\lambda\lambda}^2\frac{M_k l}{RT_e} = 2\xi\left[f_\lambda\left(\gamma t_\xi + \sum_{\alpha=1}^{\mu}\overline{c}_{\alpha\xi}H_\alpha M_\alpha + \right.\right.$$

$$\left.\left. + \frac{M_k}{RT_e}\frac{\rho_e}{\rho}u_e u_{e\xi}\right) - f_\xi\left(\sum_{\alpha=1}^{\mu}\overline{c}_{\alpha\lambda}H_\alpha M_\alpha + \gamma t_\lambda\right)\right]; \qquad (3.5.2)$$

$$(\overline{I}_{\alpha\lambda})_\lambda - f\overline{c}_{\alpha\lambda} \doteq \overline{R}_\alpha\frac{2\xi}{\rho u_e\xi_s} - 2\xi[f_\lambda\overline{c}_{\alpha\xi} - f_\xi\overline{c}_{\alpha\lambda}]; \qquad (3.5.3)$$

$$\overline{R}_\alpha = \sum_{r=1}^{l}(v''_{\alpha r} - v'_{\alpha r})k_{fr}\overline{\rho}^{m'_r}\left[\prod_{j=1}^{\mu}\overline{c}_j^{v'_{jr}} - \frac{1}{\frac{k_{pr}}{p_e^{n_r}}\left(\sum_{\alpha=1}^{\mu}\overline{c}_\alpha\right)^{n_r}}\prod_{j=1}^{\mu}\overline{c}_j^{v''_{jr}}\right]; \qquad (3.5.4)$$

$$\overline{I}_{\alpha\lambda} = \frac{l}{Pr}\sum_{\beta=1}^{\mu}M_\beta L_{\alpha\beta}\left(\overline{c}_{\beta\lambda}\sum_{\alpha=1}^{\mu}\overline{c}_\alpha - \overline{c}_\beta\sum_{\alpha=1}^{\mu}\overline{c}_{\alpha\lambda}\right), \quad \alpha = 1,...,\mu. \qquad (3.5.5)$$

The assumption concerning local similarity is one of the methods /118 of approximation for solving the system (3.5.1) - (3.5.5). At any point s the dependencies of the desired variables $(f, t, \overline{c}_\alpha)$ on ξ are assumed to be such that we can disregard their derivatives with respect to ξ. Then the right-hand sides of the equations (3.5.1) and (3.5.2) are equal to zero and equations (3.5.1) and (3.5.2) become normal differential equations. The equations of diffusion for the components (3.5.3) reduce to the normal differential equations only if we assume a frozen boundary layer ($\overline{R}_\alpha = 0$) or an equilibrium boundary layer when equations of detailed equilibrium follow from equations $\overline{R}_\alpha = 0$ (see Chapter 2, Section 2). This is because in front of $\overline{R}_\alpha$ there is a factor $2\xi/u_e\xi_s$ which clearly depends on ξ. For substantially nonequilibrium flows, disregarding the formation rate of $\overline{R}_\alpha$ components is a very rough approximation. However, for cross sections not too far from the critical point we may replace $2\xi/u_e\xi_s$ by its value at the critical point.

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In face, assuming that

$$u_e = u_{es}s + u_{e3}s^3;$$
$$\eta_w = \eta_{w0} + \eta_{w2}s^2;$$
$$\rho_w = \rho_{w0} + \rho_{w2}s^2;$$
$$r = s + r_3 s^3,$$

let us obtain

$$\frac{2\xi}{u_e \xi_s} \sim \frac{1}{2u_{es}}\left[1 - \frac{s^2}{3}\left(\frac{4u_{e3}}{u_{es}} + \frac{\eta_{w2}}{\eta_{w0}} + \frac{\rho_{w2}}{\rho_{w0}} + 2r_3\right)\right]. \qquad (3.5.6)$$

The value in brackets for small values of s differs little from 1. Let us note, for example, that in the calculation given below $2\xi/u_e\xi_s \sim 5\cdot10^{-6}$ at $\tilde{s} = 0.8$ at the same time that $1/2u_{es} \sim 3.27\cdot10^{-6}$ ($\tilde{s} = s/R_{s=0}$ where $R_{s=0}$ is the radius of curvature of the material at the critical point). In the converted assumptions, equations <u>/119</u> (3.5.1) - (3.5.3) become normal differential equations with parameters depending on the local conditions in nonturbulent flow and on the surface of the body. Thus, the equations of local similarity are the following:
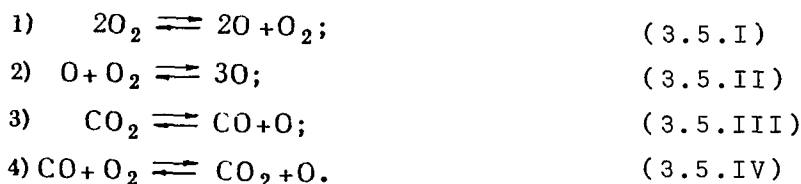
$$(lf_{\lambda\lambda})_\lambda + ff_{\lambda\lambda} + 2\left(\frac{\rho_e}{\rho} - f_\lambda^2\right)\frac{d\ln u_e}{d\ln\xi} = 0; \qquad (3.5.7)$$

$$\left(\frac{\gamma l}{p_2}t_\lambda\right)_\lambda + t_\lambda\left[f\gamma - \frac{M_k}{R}\sum_{\alpha=1}^{\mu}c_{p\alpha}\bar{I}_{\alpha\lambda}M_\alpha\right] - \sum_{\alpha=1}^{\mu}H_\alpha M_\alpha[(\bar{I}_{\alpha\lambda})_\lambda -$$

$$- f\bar{c}_{\alpha\lambda}] + u_e^2 f_{\lambda\lambda}^2 \frac{M_k l}{RT_e} = 0; \qquad (3.5.8)$$

$$(\bar{I}_{\alpha\lambda})_\lambda - f\bar{c}_{\alpha\lambda} = \bar{R}_\alpha(1/2u_{es})_{s=0}. \qquad (3.5.9)$$

It is interesting to note that all the calculations on the basis of the local similarity method, taking into account the term $u_e^2 f_{\lambda\lambda}^2 M_k l/RT_e$ in the energy equation, to a substantially lesser degree resulted in an accurate solution. Without taking into account this term the system of local similarity equations coincides formally with equations which describe the flow in the vicinity of the critical point. It is natural that the correctness of the assumption concerning local similarity depends on how slowly the parameters of the outer flow change and in fact whether the terms excluded from the equations are small in comparison with the remaining terms. We can check this only by solving the problem accurately.

We made a numerical calculation for the case of the streamline flow of a graphite sphere with oxygen O and O_2. In the gas phase the following reactions were examined:

$$1) \quad 2O_2 \rightleftharpoons 2O + O_2; \qquad\qquad (3.5.I)$$

$$2) \quad O + O_2 \rightleftharpoons 3O; \qquad\qquad (3.5.II)$$

$$3) \quad CO_2 \rightleftharpoons CO + O; \qquad\qquad (3.5.III)$$

$$4) \quad CO + O_2 \rightleftharpoons CO_2 + O. \qquad\qquad (3.5.IV)$$

Thus the gas phase consisted of a mixture of four components. We assumed that in the pores of the body only O_2 reacts since the con- /120 centration of atomic oxygen O and CO_2 on the surface of the body in the calculations was sufficiently small ($\sim 10\%$):

$$C_{graphite} + \tfrac{1}{2} O_2 \longrightarrow CO. \qquad\qquad (3.5.V)$$

In this case the velocity U_1 of the carrying away of carbon atoms as a result of the diffusion of CO from the graphite pores is written in the finite form (see Note 4, Chapter 2, Section 5)

$$U_1 = 1.4 \cdot 10^{-4} N \theta (1-\theta)^{1/2} T_w^{1/4} e^{-E/2RT_w} p_e^{1/4} \left(\bar{c}_5 \Big/ \sum_{\alpha=1}^{\mu} \bar{c}_\alpha \right)^{3/4}, \qquad (3.5.10)$$

where N is Avogadro's number, θ is the porosity and E is the activation energy of ~ 2 kCal/mole. The boundary conditions of the problem:

$$J_2 + \rho v c_2 = U_2 M_2 / N; \qquad\qquad (3.5.11)$$

$$J_3 + \rho v c_3 = 0; \qquad\qquad (3.5.12)$$

$$J_4 + \rho v c_4 = 0; \qquad\qquad (3.5.13)$$

$$J_5 + \rho v c_5 = U_5 M_5 / N; \qquad\qquad (3.5.14)$$

$$\rho v = U_1 M_1 / N; \qquad\qquad (3.5.15)$$

$$\varkappa \partial T / \partial n = \varepsilon \sigma T_w^4 - U_1 Q_5 / N, \qquad\qquad (3.5.16)$$

Here U_2 and U_5 are the formation rates of the components CO and O_2 as a result of the heterogeneous reactions. In Dorodnitsyn variables:

$$\bar{c}_2 (f \xi_s + 2\xi f_s) = r \sqrt{2\xi} \left(\bar{I}_{2\lambda} \frac{r u_e \rho_w r_w}{\sqrt{2\xi}} - \bar{U}_2 \right); \qquad (3.5.17)$$

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$$\overline{c}_3(f\xi_s + 2\xi f_s) = \overline{I}_{3\lambda} r^2 u_e \rho_w \eta_w ; \qquad (3.5.18)$$

$$\overline{c}_5(f\xi_s + 2\xi f_s) = r\sqrt{2\xi}\left(\overline{I}_{5\lambda}\frac{r u_e \rho_w \eta_w}{\sqrt{2\xi}} - \overline{U}_5\right); \qquad (3.5.19)$$

$$f = -\frac{U_1}{N} M_1 r \frac{\sqrt{2\xi}}{\xi_s} - \frac{2\xi}{\xi_s} f_s ; \qquad (3.5.20)$$

$$\frac{\gamma}{Pr} t_\lambda + \frac{Q_5\sqrt{2\xi}}{T_e R \rho_w \eta_w r u_e} = \frac{\varepsilon \sigma T_w^4 M_1 \sqrt{2\xi}}{\eta_w \rho_w r u_e R T_e}. \qquad (3.5.21)$$

We took the conditions at the outer limit from Lun'kin and Popov [44] who examined the streamline flow of a sphere by a chemically nonequilibrium ideal gas (oxygen). In the numerical calculations the distributions $\overline{c}_{\alpha e}$, p_e and T_e were approximated on the basis of s polynomials of the fourth power. The streamline flow conditions: /121 $M_\infty = 10$, $p_\infty = 0.01$ atm and $T_\infty = 290°$ K. At the critical point of the body $p_e = 1.315$ atm, $T_e = 3297°$K and $c_4 = 0.1199$. We took the radius of the sphere as equal to 1 cm. To solve the system of equations (3.6.1) - (3.6.5) in special derivatives a linear method with a different scheme of the second order of accuracy with respect to $\tilde{s}$ and λ was selected. To calculate the derivatives of $\tilde{s}$ in the i-th cross section we must know the desired functions in the i, i-1 and i-2 cross sections. In zero approximation the distribution of functions in the i-1 section is communicated to the i-th layer. The obtained system of normal nonlinear differential equations was solved with the use of iteration. At each iteration the values of the derivatives of the desired functions with respect to $\tilde{s}$ was corrected. The described solution method gave rise to varying instability. The stability of the analysis was ensured by introducing a damping coefficient on the basis of the formula [cf. (3.4.1)]

$$\varphi_{in}^{'(s)} = \varphi_{i,n-1}^{'(s)} + \delta^{(s)}(\varphi_{in}^{(s)} - \varphi_{i,n-1}^{'(s)}), \qquad (3.5.22)$$

where $\phi_{in}^{(s)}$ is the value of the desired function ϕ_i in the s-th cross section obtained in the n-th iteration and $\phi_{in}^{'(s)}$ is the value of this function used in the $(n+1)$-th iteration. The value of the coefficient $\delta^{(s)}$ changed in the range from 0.1 at $\tilde{s} = 0$ to 0.01 at $\tilde{s} = 1$. We performed the numerical calculation up to $\tilde{s} = 1$ since the solution to the outer nonequilibrium problem is in the work of Lun'kin and Popov [44]. Let us note that the critical point is singular. To escape from it we must generally apply the series expansion of the desired functions with respect to $\tilde{s}$. However, in this calculation we applied the results of the calculation for $\tilde{s} = 0$ to the first layer. As we have explained, moving the solution at the critical point to the first layer in the first step
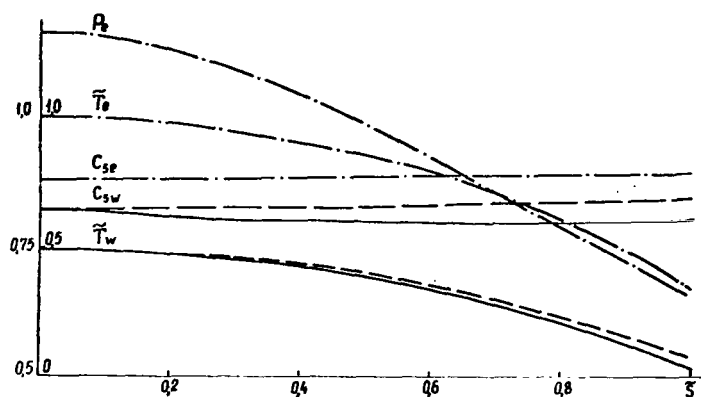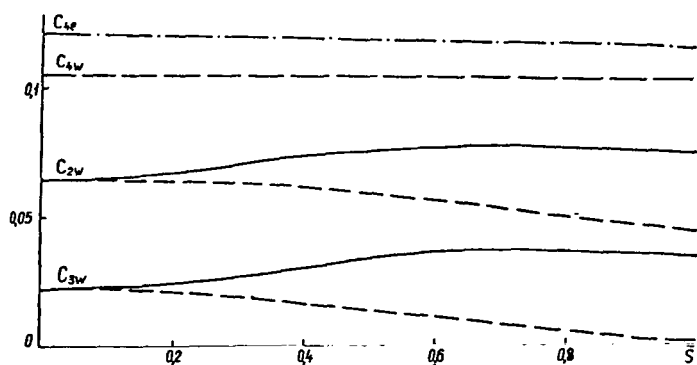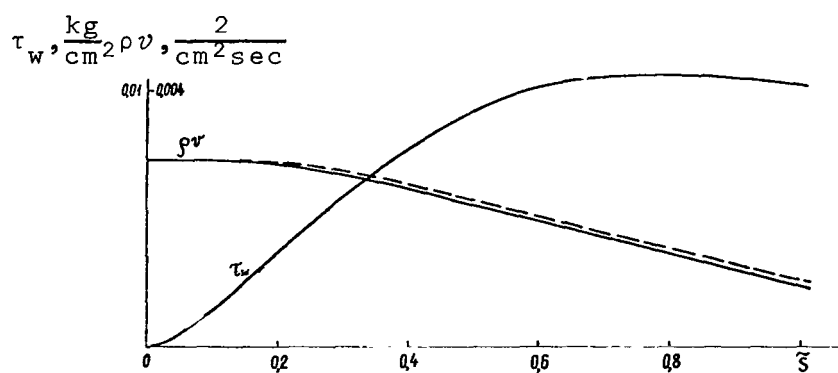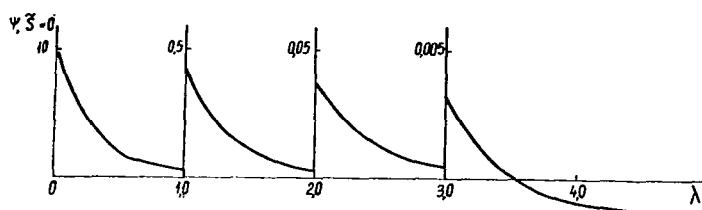
Fig. 33

Fig. 34

$$\tau_w, \frac{kg}{cm^2} \rho v, \frac{2}{cm^2 sec}$$

Fig. 35

Fig. 36

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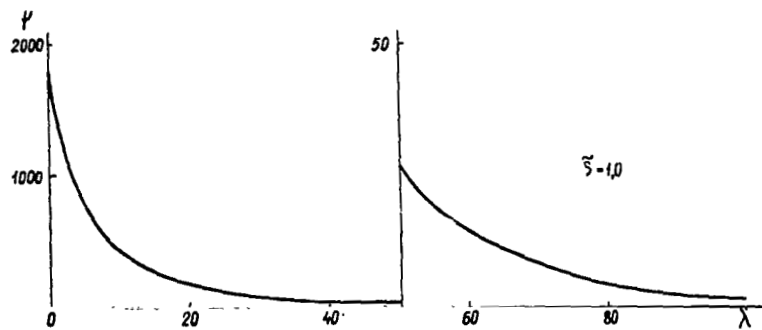
Fig. 37
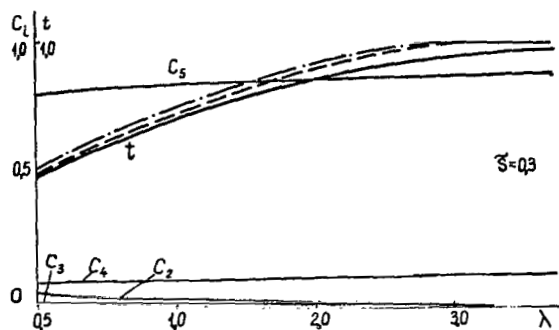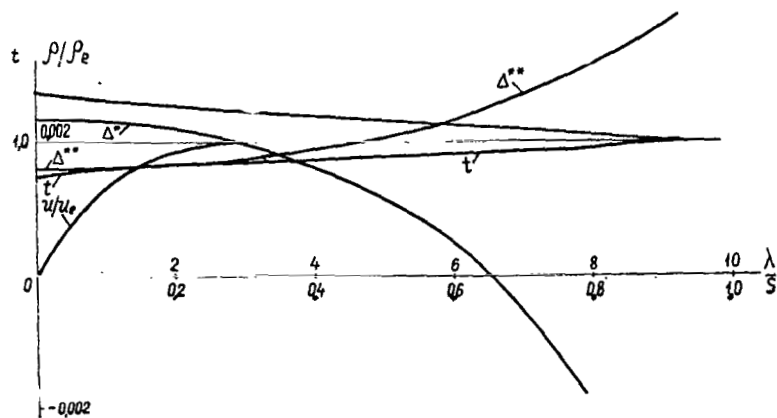
Fig. 38

Fig. 39

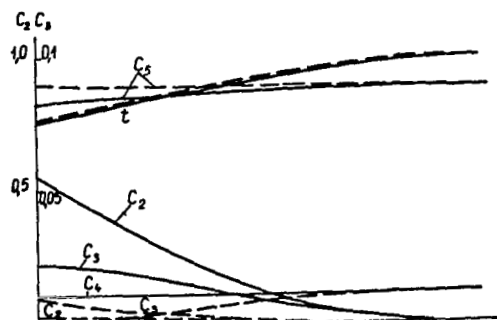Fig. 40

$\tilde{s} = 0.1$ does not cause any substantial error in the solution. The calculation was performed in the variables λ and s' so that equations (3.5.1) - (3.5.5) became integral-differential; the integrals were found on the basis of the Simpson formula. The calculation across the boundary layer was performed with a constant interval equal to 0.1 up to $\lambda = 10$.

In Figure 33 we have given the distributions $\tilde{T}_e$, $\tilde{T}_w$, P_e, c_{5e} and c_{5w} (here we have introduced the symbol $\tilde{T} = T/T_{e,s=0}$) and in Figure 34 we have given the distributions c_{4e}, c_{4w}, c_{2w} and c_{3w}. The dashed line represents the solution obtained on the basis of the local similarity method, and the distributions of the values p_e, $\tilde{T}_e$, c_{4e} and c_{5e} at the outer limit of the boundary layer are drawn by a dash-dot line. Let us find the friction stress on the wall: /124

$$\tau_w = (\eta \partial u/\partial y)_{y=0} = \rho_w \eta_w u_e^2 (f_{\lambda\lambda})_{\lambda=0} r/\sqrt{2\xi}. \qquad (3.5.23)$$

In Figure 35 we have given τ_w and $(\rho v)_w$ on the surface of the body. The local similarity method in this problem coincides satisfactorily $(\rho v)_w$ with the accurate solution ($\sim 13\%$ at $\tilde{s} = 1.0$) but elevates the surface temperature somewhat. The distributions of $c_{\alpha w}(\tilde{s})$ differ substantially from those obtained in the precise solution. Let us note that a slight decrease (with the increase of $u_e(\tilde{s})$ to $\tilde{s} = 1$ inclusive) of τ_w at $\tilde{s} = 1.0$ is due to the substantial drop in the values of ρ_w and η_w as a result of the decrease in surface temperature. In Figure 36 and 37 we have drawn on a discontinuous scale the function Ψ which characterizes the deviation from local equilib-

rium [$\Psi = \left(\overline{c}_4^2 p_e / \overset{\mu}{\underset{\alpha=1}{\Sigma}} \overline{c}_\alpha \overline{K}_{p_1} \right) - \overline{c}_5$] for the cross sections $\tilde{s} = 0$

and $\tilde{s} = 1.0$. Here K_{p_1} is the equilibrium constant of the reactions (3.5.I) and (3.5.II). We can easily see that with an increase in $\tilde{s}$ the deviation from local equilibrium in this problem is increased substantially. As we have mentioned in taking into account the term $u_e^2 f_{\lambda\lambda}^2 M_k l/RT_e$ in the energy equations in calculations on the basis of of the local similarity method the results were less accurate. As an example in Figure 38 we have given the functions $c_\alpha(\lambda)$ and $t(\lambda)$ for $\tilde{s} = 0.3$. The solid lines correspond to the precise solution, the dash-dot lines indicate that the term $u_e^2 f_{\lambda\lambda}^2 M_k l/RT_e$ has been taken into account and the dashed lines, that it has not. In Figure 39 we have drawn the displacement thicknesses and the pulse losses Δ^*, Δ^{**}. It is interesting to note that $\Delta^*(\tilde{s})$ is a diminishing function which assumes negative values at sufficiently large values of $\tilde{s}$. This is because the density within the boundary layer was more than at the outer limit of the layer. Nevertheless, at large values of $\tilde{s}$ the dynamic boundary layer is substantially

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thinner than the temperature boundary layer. As an example we have given in Figure 39 the functions $\rho(\lambda)/\rho_e u(\lambda)/u_e$ and $t(\lambda)$ for $s = 0.8$ [see (3.4.41) - (3.4.44) for values of Δ^* and Δ^{**}]. Finally, in Figure 40 we have compared the calculation of the frozen boundary layer at the critical point. The dashed lines represent the frozen boundary layer. In calculating the frozen boundary layer we have assumed the state of the gas at the wall to be equilibrium. In accordance with this the boundary conditions of (3.5.11) - (3.5.14) were replaced by the following conditions:

$\bar{c}_5 = (\bar{c}_3/\bar{c}_2)\sum\limits_{\alpha}^{2}\bar{c}\bar{K}_{p6}$ where $\bar{K}_{p6}$ is the equilibrium constant of the reaction

$$2CO + O_2 \rightleftharpoons 2CO_2; \qquad\qquad (3.5.VI)$$

$$\bar{c}_4 = 0, \quad \sum\limits_{\alpha}\bar{c}_\alpha M_\alpha = 1, \quad \bar{I}_{2\lambda} + \bar{I}_{3\lambda} = -f\left(\frac{1}{M_1} - \bar{c}_2 - \bar{c}_3\right).$$

Let us note the great difference in the distribution of concentra- <u>/125</u> tions across the boundary layer in frozen and nonequilibrium flows.

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